Studies in Phase Equilibria, Polymorphism and Solid Phase Reactions

Thesis presented for the Degree of Doctor of Science

by

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University of Edinburgh

April 1955

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11. The Oxygen Absorption of Rubber Vulcanisates in Light: S. Horrobin, R. G. A. New and Duncan Taylor, Transactions of the Faraday Society, 1946, 42, 252-257.

12. An Inexpensive Thermostat Relay: Duncan Taylor, Journal of the Chemical Society, 1951, 232-233.

Studies in Phase Equilibria, Polymorphism and Solid Phase Reactions.

Introduction.

The investigations described in this thesis deal initially with phase equilibria in inorganic and organic systems. This work led subsequently to the study of polymorphism and the kinetics of polymorphic transformations and thence to the study of solid reactions in general.

Of the twelve communications here presented, the first four concern investigations of phase equilibria in metal sulphate-sulphuric acid-water systems, the metals being manganese, aluminium, iron and chromium. The main achievements included the unambiguous identification of solid phases and the determination of solubilities and isothermal invariant points, from which the polythermal diagrams for the various systems were constructed. Stress is laid on the necessity for highly accurate analytical work, particularly in the aluminium and chromic sulphate systems, and the need for supplementing such data by microscopic and X-ray examination of solid phases. The use of a radio-active tracer to assist in the identification of solid phases is particularly well

illustrated in the case of the aluminium sulphates. From the polytherm for the manganous sulphate system, a graphical procedure was devised for distinguishing between normal sulphate hydrates and acid sulphates. This is valuable since both types of compound frequently occur in these systems, a fact which has in the past led to confusion regarding the true nature of the solid phases. The application of the graphical procedure is illustrated in the aluminium sulphate system, where an unusual range of highly hydrated acid sulphates occurs and where the equilibria are complicated by the occurrence in the solid phases of inter-crystallite liquid and of lattice defects. The chromic sulphate system on the other hand does not show a parallel series of acid sulphates, although it is clear that in the acid sulphate $Al_2(SO_4)_3$, H_2SO_4, $2H_2O$, using suitable methods of preparation, a maximum of about 30% of the aluminium can be replaced by chromium without changing the lattice structure.

In the fifth paper, similar objectives together with the determination of three-phase data were attained for several sulphonic acid-water systems. A characteristic feature is the formation of stable sulphonic acid monohydrates, whose structures are best regarded as ionic, of the type $R.SO_3^-H_3O^+$. This suggestion is in agreement with recent work on the nuclear magnetic properties of

similar monohydrates. Numerous other hydrates of lower stability were identified, and by utilising the three-phase data a procedure is suggested for the calculation of heats of dissociation of hydrates, which is independent of the determination of dissociation pressures.

The application of phase equilibria technique (with the use of a Kofler hot-stage microscope) in the study of polymorphism and liquid crystal formation in azo- and azoxy-compounds is exemplified in the sixth paper, and this is extended in the seventh to the cis-trans isomerism of azo-compounds. In the latter paper, other physical methods (X-ray powder photographs, absorption spectra and dipole moment determinations) are included. This work definitely established the existence of some hitherto unknown cis-azopyridine compounds, and showed that cis-azobenzene is a distinct geometrical isomer and not, as had been suggested, a compound of azoxybenzene with hydrazobenzene. Many examples of polymorphism in the azo-series are also described. The instrument used for the measurement of dipole moments is described in the eighth paper.

In the above work on polymorphism, one example, namely azoxybenzene, showed promise of being eminently suitable for the study of the kinetics of polymorphic transformations under thin film conditions. A detailed study of one of the azoxybenzene processes, a photometric method for the

measurement of transformation rates being used, is given in the ninth paper. The transformation is shown to be closely parallel to the monoclinic→rhombic sulphur case, in that the mechanism is based on the differential escape of molecules from the two adjacent lattices, and requires the full heat of sublimation of the metastable form as energy of activation. The temperature independent factor of the rate is very large, indicating that the thermal activation of one molecule with energy equivalent to the heat of sublimation leads to the transformation of c.10^9 molecules, a number which corresponds with the usual estimates of the size of a mozaic block. This behaviour can be accounted for on the basis of a mosaic block theory, according to which the transformation occurs with low energy of activation over small elements of volume (i.e. mozaic blocks) and a much higher energy is required to "bridge" adjacent blocks. If the bridges are formed by condensation of molecules from the vapour phase, the higher energy of activation will be approximately equal to the heat of sublimation and will determine the temperature coefficient of the transformation.

Polymorphic transformations represent the simplest type of solid reaction being of the form solid 1→ solid 2. A more complicated case is the type solid 1→ solid 2 + gaseous products, an example of which is described in the tenth paper.

Here, the thermal decomposition of ammonium dichromate is shown to occur in two main stages: an autocatalytic process of the Prout-Tompkins type, followed by a linear interface reaction. The decomposition appears to be determined both by crystallographic and chemical properties.

The eleventh paper describes work on the oxidation of rubber vulcanisates, for which a free radical chain mechanism is proposed, and the last communication gives the circuit diagram of a simple robust electronic relay used throughout the phase studies for the control of thermostats.

In conclusion, the author records his gratitude to his research collaborators, without whose assistance important sections of the experimental work could not have been carried out.

Preprinted from the Journal of the Chemical Society, June 1952, (444), pages 2370—2375.

444. *The System* $MnSO_4$–H_2SO_4–H_2O.

By Duncan Taylor.

The system $MnSO_4$–H_2SO_4–H_2O has been investigated at 0°, 20°, 25°, 45°, 65°, and 95·7°, and the following succession of solid phases observed: $MnSO_4,5H_2O$, $MnSO_4,H_2O$, $MnSO_4,H_2SO_4,H_2O$, $MnSO_4,H_2SO_4$, and $MnSO_4,3H_2SO_4$. The pentahydrate does not exist in contact with saturated solutions above 24·5°, and the lower formation temperature of $MnSO_4,H_4SO_4$ is very close to 65°. The microscopical appearance of solid phases together with details of solubility measurements and analytical procedures are given. Conditions under which transitions between hydrates and/or acid sulphates occur in condensed sulphate systems have been examined, and lead to an empirical method for distinguishing between normal and acid sulphates whether hydrated or not.

Solid–liquid phase equilibria in condensed metal sulphate–sulphuric acid–water systems may show one or both of two general features: (*a*) progressive dehydration of normal sulphate hydrates as the temperature is raised and/or the acid concentration increased, and (*b*) formation of acid sulphates. Polythermal equilibrium data provide comparisons of hydrate–lower hydrate, hydrate–acid sulphate and acid sulphate–higher acid sulphate transitions and, while reliable results for (*a*) are numerous, examples of (*b*) either alone or in conjunction with (*a*) have received much less attention. Manganese sulphate is one such case, only one isotherm at 12·6° having been reported (Montemartini and Losana, *Ind. chim., Roma*, 1928, **4**, 107). The following succession of solid phases with increasing acid concentration is claimed: $MnSO_4,5H_2O$, $MnSO_4,4H_2O$, $MnSO_4,H_2O$, $MnSO_4$, $MnSO_4,H_2SO_4,H_2O$, $MnSO_4,H_2SO_4$, $MnSO_4,3H_2SO_4$. Data for this system over the range 0—95·7° are now presented, and the above three types of transition compared for this and other systems for which sufficient reliable data are available.

Experimental

"AnalaR" materials were used throughout, the manganese sulphate being in the form of the metastable tetrahydrate (B.D.H.). Mixtures of the desired composition were prepared from previously analysed materials by weighing in small tubes or flasks. These were closed with rubber stoppers carrying glass stirrers and 6″ stirrer glands lubricated with stiff grease. Thus absorption of atmospheric moisture by the solutions during stirring to equilibrium was negligible. The time to reach equilibrium varied from a few hours at 95·7° to a fortnight at low temperatures and high acid concentrations. Owing to comparatively small changes in solubility with temperature and the absence of marked supersaturation, it was not possible to bring the initial tetrahydrate solid phase completely into solution before transference to the thermostat bath, but fortunately inter-solid phase transitions were moderately rapid and progress towards equilibrium could be readily observed by microscopical examination. The establishment of equilibrium was judged both microscopically and by agreement between solubility results for duplicate experiments. Electrically heated water-thermostats controlled within ±0·02° by electronic relays (Taylor, *J.*, 1951, 232) were used at 20°, 25°, 45°, and 65°, gas heating at 95·7° ± 0·2°, and a well-lagged bath of melting ice at 0°. A layer of liquid paraffin minimised evaporation at the higher temperatures. Samples of saturated solutions were withdrawn for analysis by means of a pre-heated micro-filter stick of No. 3 porosity and a pipette of suitable volume; the samples were weighed in a closed vessel and diluted to a standard volume with distilled water. When a sample of the moist solid phase was required, as much as possible of the remaining liquid was removed with water-pump suction *via* the filter stick without removal of the solubility vessel from the thermostat. Since all the solid phases were well crystallised and settled rapidly, this sampling procedure could be carried out so quickly that absorption of moisture by the deliquescent phases was negligible except at very high acid concentrations at 95·7°. Even then absorption was very slight.

Although none of the crystals except $MnSO_4,5H_2O$ and $MnSO_4,H_2O$ could be isolated in the dry state for refractive index measurements, the appearance and optical properties of all of them when viewed, in contact with mother-liquor, with a polarising microscope were sufficiently characteristic to allow of their certain identification. These observations always agreed with tie-line information, and thus analyses of moist solid phases could frequently be dispensed with. Indeed, isothermal invariant points could be recognised with complete certainty microscopically, but not so from tie-lines unless the two solid phases were present in roughly equal amounts.

Analytical Procedure.—The samples were analysed for manganese and free sulphuric acid, water being determined by difference. For manganese, the bismuthate procedure (Vogel,

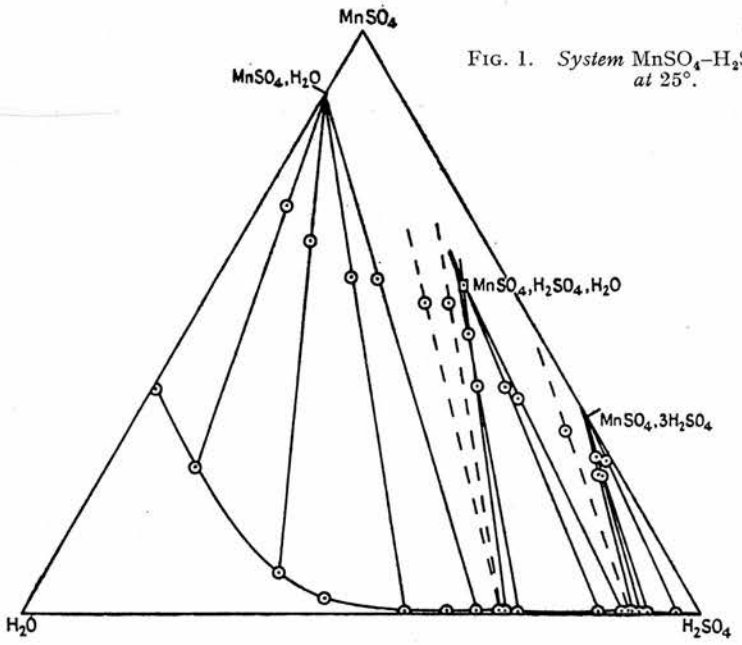


FIG. 1. *System* $MnSO_4$–H_2SO_4–H_2O *at* 25°.

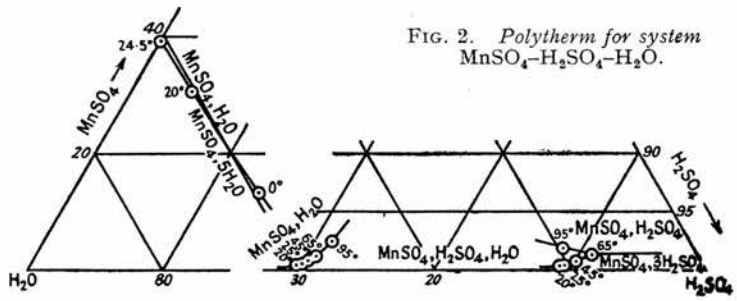


FIG. 2. *Polytherm for system* $MnSO_4$–H_2SO_4–H_2O.

" Quantitative Inorganic Analysis," Longmans, Green & Co., 1948, p. 358) was shown to be accurate over the range of manganese concentrations and of $MnSO_4$: H_2SO_4 ratios encountered in this work if 15 minutes were allowed for the oxidation at room temperature. Typical results with standard potassium permanganate solution reduced with sulphur dioxide as a known source of manganese are shown in Table 1. For sulphuric acid, titration with standard sodium carbonate solution and a bromocresol-green–methyl-red mixed indicator proved highly accurate provided carbon dioxide was removed by boiling just before the true end-point. Since the latter is delayed when carbonate is run into an acid solution, a preliminary titration was necessary. The indicator contained 0·09 g. of bromocresol-green and 0·06 g. of methyl-red in 100 ml. of 80% alcohol, and changed from bluish-pink through grey to green with increasing pH. The very sharp grey-to-green change was always taken as the end-point. Results for known H_2SO_4–$MnSO_4$ mixtures are given in Table 1.

TABLE 1.

Taken: $MnSO_4$, mg.	Taken: Wt.-ratio H_2SO_4 : $MnSO_4$	Found: $MnSO_4$, mg.	Taken: 0·5N-H_2SO_4, ml.	Taken: Wt.-ratio $MnSO_4$: H_2SO_4	Found: 0·5N-Na_2CO_3, ml.
6·04	1000	5·93	25·0	0·0	25·00
30·2	100	30·08	25·0	0·048	24·99
75·5	0	75·53	25·0	0·96	24·99
151·0	0	151·4	25·0	4·8	25·01
			25·0	9·6	25·00
			25·0	14·4	25·00

RESULTS.

Microscopical Appearance of Solid Phases.—$MnSO_4,5H_2O$ is pink, triclinic, with the same habit as that of perfectly formed $CuSO_4,5H_2O$ crystals (cf. Hammel, *Ann. Chim.*, 1939, **11**, 247). $MnSO_4,H_2O$ forms minute birefringent bipyramids or four-sided prisms which in bulk appear almost white. $MnSO_4,H_2SO_4,H_2O$ forms 1—2-mm., pink, six-sided plates whose opposite edges and side faces are parallel, none of the side faces being perpendicular to the plane of the hexagon. Extinction is symmetrical and multiple twinning frequent. The acute bisectrix is

TABLE 2. *The System* $MnSO_4$–H_2SO_4-H_2O.

Solution $MnSO_4$, %	Solution H_2SO_4, %	Moist solid phase $MnSO_4$, %	Moist solid phase H_2SO_4, %	Extrapolated tie-lines, $MnSO_4$, %	Solid phase
At 0°.					
13·10	27·90	—	—	—	A + B
At 20°.					
30·61	8·98	—	—	—	A + B
0·47	69·64	—	—	—	B + C
0·37	89·09	—	—	—	C + D
At 24·5°.					
* 39·3	0·0	—	—	—	A + B
At 25°.					
38·81	0·23	—	—	—	B
25·08	12·98	70·0	3·92	89·45	B
7·07	34·34	63·95	10·43	88·71	B
2·71	43·26	—	—	—	B
0·58	56·18	57·93	19·52	88·49	B
0·39	62·39	—	—	—	B
0·41	66·90	57·62	23·55	88·7	B
0·53	70·09	53·32	36·06	83·2	B + C
0·53	70·00	53·26	32·54	99·1	B + C
0·42	70·90	48·21	41·50	74·9	C
0·28	72·89	39·1	47·50	77·87	C
0·19	84·90	39·04	51·57	99·1	C
0·33	88·20	36·94	54·50	96·2	C
0·42	89·30	31·41	64·20	54·5	C + D
0·34	89·54	23·93	72·80	35·2	D
0·20	90·90	27·00	71·00	34·78	D
0·09	92·08	23·73	73·60	35·95	D
0·02	96·29	26·24	72·91	34·10	D
At 45°.					
38·49	0·0	—	—	—	B
18·40	19·54	—	—	—	B
2·63	44·75	—	—	—	B
5·22	62·20	—	—	—	B
0·81	70·30	—	—	—	B + C
0·25	77·70	—	—	—	C
0·27	83·80	—	—	—	C
0·74	90·02	—	—	—	C + D
0·75	90·05	—	—	—	C + D
0·41	91·59	—	—	—	D
0·08	96·92	—	—	—	D

Solution $MnSO_4$, %	Solution H_2SO_4, %	Moist solid phase $MnSO_4$, %	Moist solid phase H_2SO_4, %	Extrapolated tie-lines, $MnSO_4$, %	Solid phase
At 65°.					
35·88	0·0	—	—	—	B
16·78	20·40	—	—	—	B
2·87	45·93	—	—	—	B
0·89	61·73	—	—	—	B
1·26	70·70	—	—	—	B + C
0·54	76·10	—	—	—	C
0·44	83·41	—	—	—	C
0·94	89·20	38·65	53·44	95·07	C
1·35	90·70	—	—	—	C + E
1·31	90·80	43·91	54·34	56·07	E
1·30	90·91	—	—	—	E + D
1·04	91·68	24·93	72·90	35·07	D
0·72	92·79	—	—	—	D
At 95·7°.					
25·87	0·0	—	—	—	B
2·06	69·41	59·39	24·06	89·79	B
2·48	71·20	—	—	—	B + C
2·11	72·28	40·20	47·26	76·75	C
1·70	88·40	37·25	54·60	94·68	C
1·89	88·50	45·19	51·70	65·92	C + E
1·79	89·15	45·20	52·27	62·07	E
1·61	90·58	—	—	—	E
1·52	91·41	—	—	—	E
1·43	92·40	42·44	55·30	66·17	E
1·38	93·0	—	—	—	E
1·35	93·63	44·70	53·59	67·10	E
1·34	94·49	44·16	54·21	71·61	E
1·39	95·87	47·18	51·80	74·36	E

* Krepelka and Rejha, *Coll. Czech. Chem. Comm.*, 1933, **5**, 67.

Solid phases: A = $MnSO_4,5H_2O$
B = $MnSO_4,H_2O$
C = $MnSO_4,H_2SO_4,H_2O$
D = $MnSO_4,3H_2SO_4$
E = $MnSO_4,H_2SO_4$

almost perpendicular to the plate, the optic axial angle is small, and the optical sign negative. $MnSO_4,H_2SO_4$ occurs as very small pink birefringent parallelepipeds or short six-sided prisms with several end faces. $MnSO_4,3H_2SO_4$ forms highly birefringent four-sided prisms which are biaxial negative, with the slow ray across the prism. Extinction is not symmetrical.

Phase Equilibria.—Table 2 contains all the solubility and tie-line measurements, the column headed " Extrapolated tie-lines, $MnSO_4$, % " giving the points where the mathematically extrapolated tie-lines cut either the $MnSO_4$–H_2O or the $MnSO_4$–H_2SO_4 side of the equilateral triangle as the case may be. These points have direct significance regarding the composition of solid phases B, D, and E (theor. : 89·3, 33·9, and 60·6% of $MnSO_4$ respectively), but not for the ternary compound C whose composition must be judged from the appropriate tie-line convergence point inside the triangle. Compositions are by weight. Typical tie-line convergence is shown on the 25° isotherm in Fig. 1, and the polytherm projection diagram in Fig. 2. The $MnSO_4,H_2SO_4$–$MnSO_4,3H_2SO_4$ isothermal invariant point at 95·7° is unknown, but the corresponding univariant line on the polytherm must run from the lower formation point of $MnSO_4,H_2SO_4$ passing very near to the last point on the 95·7° isotherm. This is the direction given in Fig. 2.

Discussion

In view of (1) the presence of not more than 30% of liquid phase in samples of moist solid phases, (2) the reliability of the analytical procedures, and (3) the use of mathematical extrapolation to eliminate drawing errors, the position of the tie-lines is considered accurate in all cases except at very high acid concentrations at 95·7°. The composition of the solid phases B, C, and D as deduced from tie-line convergence is, therefore, quite unambiguous, but this is not so for the solid E. Composition $MnSO_4,H_2SO_4$ for E is, however, preferred on several grounds. The relevant tie-lines should converge for this composition at the point $MnSO_4$ 60·6% on the $MnSO_4$–H_2SO_4 side of the triangle, and the most reliable line, *i.e.*, that which makes the largest angle with this side, does in fact run to the point 62·07% (see Table 2), while the tie-line from the neighbouring invariant solution runs to the point 65·92%. The latter implies that the solid E must contain less than 65·92% $MnSO_4$ and could not, therefore, be $MnSO_4$ or $2MnSO_4,H_2SO_4$. That four of the tie-lines in question do actually run to points with higher $MnSO_4$ contents is believed due to the fact that they run almost parallel to the $MnSO_4$–H_2SO_4 side of the triangle, and in consequence errors as small as 0·2% in the water content of the moist solid phase points would have a major effect on the gradient of the corresponding tie-lines. The observed displacement of the latter from convergence at $MnSO_4$ 60·6% is consistent with the absorption of about 10 mg. of water by the moist solid phases during sampling and this is considered not improbable. It is unlikely that the displacement is due to the presence in addition to E of a second solid phase, *viz.*, $MnSO_4$ or $2MnSO_4,H_2SO_4$, because (1) the solid phase was microscopically homogeneous, (2) experiment showed that the anhydrous sulphate, prepared by heating the pentahydrate *in vacuo* at 200° (controlled by analysis), is rapidly converted into E when heated with 98·6% H_4SO_2 at temperatures between 95° and the boiling point, and (3) true equilibrium was undoubtedly established and there could, therefore, be no question of E's slowly changing into another phase. Furthermore, the composition $2MnSO_4,H_2SO_4$ for E would require the moist solid phases to contain about 40% of mother-liquor, but, in view of the well-crystallised nature of E and the method of sampling, the figure 25% as required by $MnSO_4,H_2SO_4$ is considered much more probable. Little significance can be attached to the 65° tie-line for E, which runs to $MnSO_4$ 56%, owing to the extremely small range of stability of E at this temperature. The solid phase in this instance may have contained a small amount of phase D which would account for the low $MnSO_4$ content.

There is no evidence for the occurrence as stable solid phases of the tetrahydrate or anhydrous normal sulphates as reported by Montemartini and Losana (*loc. cit.*) at 12·6°. As mentioned above, $MnSO_4,H_2SO_4$ is still present as stable solid phase in 98% acid even at the boiling point, and it seems unlikely, therefore, that the anhydrous normal sulphate ever appears in the ternary system at atmospheric pressure. These authors also claim the existence of $MnSO_4,H_2SO_4$ at 12·6°, but from Table 2 it is clear that the lower formation temperature of this phase is only very slightly less than 65°. The present solubility results

differ considerably from those of the authors mentioned. All the moist acid sulphate phases dissolved in water with evolution of heat greatly in excess of that due to adhering mother-liquor alone, thus suggesting the presence of covalent H_2SO_4 molecules (or $H_3O^+HSO_4^-$ in the case of $MnSO_4,H_2SO_4,H_2O$) as structural units in the lattices.

It will be seen from Fig. 2 that the water content of all points on the univariant line where $MnSO_4,5H_2O$ and $MnSO_4,H_2O$ co-exist in contact with saturated solutions increases with rise in temperature. This behaviour is common to all inter-hydrate transitions in systems showing the feature (*a*) mentioned above for which reliable data are available (a total of 18 examples) and may therefore be considered characteristic of this type of transition. An alternative statement of this water requirement is that, on traversal of the hydrate saturation surfaces at constant water content in the direction of rising temperatures, the path must pass from a higher to a lower hydrate surface and never the reverse. It is noteworthy that the transition $MnSO_4,H_2SO_4,H_2O \rightleftharpoons MnSO_4,H_2SO_4$ involving acid sulphates also conforms to the water condition, as does a similar example in the ferric sulphate system.

Analogously, for this and other systems showing feature (*b*), paths over the acid sulphate saturation surfaces at constant sulphuric acid content in the direction of rising temperature always pass from a higher to a lower acid sulphate surface. This corresponds to a rise in the free acid content of all points on the univariant lines with rise in temperature. Thirteen examples have been found altogether. The transitions $MnSO_4,H_2O \rightleftharpoons MnSO_4,H_2SO_4,H_2O$ and $MnSO_4,H_2SO_4,H_2O \rightleftharpoons MnSO_4,3H_2SO_4$, and a similar example from the ferric sulphate system, also conform to the acid sulphate case.

It appears therefore that the direction of the appropriate univariant lines could be used to characterise the three types of transition, and thus to distinguish between normal and acid sulphates, whether hydrated or not, in cases where tie-line convergence is ambiguous. Corresponding transitions in systems of the type M_2O–P_2O_5–H_2O, though only a few examples are available, appear to conform to the same criteria as apply in sulphate systems. In MCl–HCl–H_2O systems only a minority of hydrate transitions conform.

Grateful acknowledgments are made to Professor H. Bassett for much stimulating correspondence, and to Imperial Chemical Industries Limited and the Moray Endowment Fund for grants for chemicals and apparatus. Part of this work was carried out during the tenure of an I.C.I. Fellowship.

UNIVERSITY OF EDINBURGH. [*Received, February 25th*, 1952.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

(*Reprinted from Nature, Vol.* 168, *p.* 520, *September* 22, 1951)

Solid Phase Determinations in the System Aluminium Sulphate/Sulphuric Acid/ Water using Tracer Technique

In the system aluminium sulphate/sulphuric acid/water, the solid phase in the range 50–60 per cent sulphuric acid has been reported to be either $Al_2(SO_4)_3.9H_2O$ [1,2] or $Al_2(SO_4)_3.10H_2O$ [3] at temperatures between 20° and 60°, the composition of this solid being deduced by the Schreinemakers[4] method of tie-line convergence. However, in view of (*a*) the high molecular weight of aluminium sulphate compared with sulphuric acid and water, (*b*) the relative position in the equilateral triangle of the solubility curve, (*c*) inaccuracy in the position of the solution and moist solid points owing to the well-known difficulty of determining sulphuric acid in presence of aluminium sulphate, the published tie-lines show equally good convergence at points representing the 8, 9 or 10 hydrates or the 1 : 1 acid sulphate with eleven to thirteen molecules of water of crystallization.

This and similar cases[5] of ambiguity may be resolved by adding to the solubility mixture a suitable indicator substance which remains throughout in the liquid phase. Provided this indicator does not significantly alter the phase equilibrium and can be determined accurately in trace quantities, then the composition of the moist solid phase can be corrected for the contaminating liquid phase. Radioactive cæsium sulphate has been found to fulfil these severe conditions very well: only 0·05 c.c. of 0·045 per cent aqueous solution of approximately 15 μC. activity was required in a 50-gm. solubility mixture. This was not added until after the ternary mixture had been brought to equilibrium at 30° to avoid any co-precipitation of the tracer with the solid phase. The saturated solution and moist solid phase after convenient dilution were analysed for aluminium by precipitation with 8-hydroxyquinoline, for sulphuric acid by an accurate titration procedure, while counts were carried out in Type *M*6 Geiger–Müller liquid counters. Self-absorption errors were negligible because the counted solutions, after dilution with an equal volume of water, gave exactly half the original count. The solid phase was shown in this way to have the composition 51·4 per cent $Al_2(SO_4)_3$, 15·9 per cent H_2SO_4, 32·7 per cent H_2O, and must therefore be $Al_2(SO_4)_3.H_2SO_4.12H_2O$. This composition has been confirmed by using trace quantities of manganous sulphate as indicator, the manganese being determined colorimetrically as permanganate. The

Preprinted from the Journal of the Chemical Society, November 1952, (850), pages 4431—4442.

850. *The System* $Al_2(SO_4)_3$–H_2SO_4–H_2O.

By Duncan Taylor and (in part) Henry Bassett

Improved analytical methods being used, the system $Al_2(SO_4)_3$–H_2SO_4–H_2O has been investigated by phase-rule methods at 25°, 30°, 50°, and 60°, and the following solid phases have been found : $Al_2(SO_4)_3,16H_2O$, which habitually contains about half a molecule of additional water held by adsorption or in a zeolitic manner; $Al_2(SO_4)_3,14H_2O$; $2Al_2(SO_4)_3,H_2SO_4,24H_2O$; $Al_2(SO_4)_3,H_2SO_4,12H_2O$; $Al_2(SO_4)_3,H_2SO_4,8H_2O$ in two forms, the metastable one of which contains a slight excess of acid; $Al_2(SO_4)_3,H_2SO_4,2H_2O$, which contains a slight excess of acid and water. Anhydrous $Al_2(SO_4)_3$ with and without a slight excess of acid and water, $Al_2(SO_4)_3,H_2SO_4,2H_2O$, $Al_2(SO_4)_3,9H_2O$, and $Al_2(SO_4)_3,6H_2O$ have been prepared in other ways. All these solids have been isolated in the dry state for analysis, and in a search for isomorphism their *X*-ray powder photographs have been compared with those of the mineral coquimbite, of corresponding ferric sulphates, and of ferric ammonium sulphate and its tetrahydrate. Solubilities, microscopical appearances, and lattice spacings are recorded. The nature of the non-stoicheiometric solid phases and the application of Taylor's criteria (*J.*, 1952, 2370) for distinguishing between normal and acid sulphates are discussed. Certain results for the $Al_2(SO_4)_3$–H_2O system are included.

The investigation by phase-rule methods of systems of the type metal sulphate–sulphuric acid–water can furnish valuable data regarding the hydrates of the metal sulphate and the occurrence of acid sulphates (cf. Taylor, *J.*, 1952, 2370). In the case of aluminium sulphate, 13 hydrates of the normal sulphate containing from 2 to 27 molecules of water of crystallisation, together with six acid sulphates varying from 1,1,3 [$\equiv Al_2(SO_4)_3,H_2SO_4,3H_2O$, a convention which is used throughout this paper] to 1,3,12 have been reported, but it seems very doubtful if all of these are in fact distinct chemical individuals, and furthermore, little information is available regarding the conditions under which they are stable (Mellor, " Inorganic and Theoretical Chemistry," Longmans, 1924, **5**, p. 332). Recent ternary solubility work has failed to clarify this position. Henry and King (*J. Amer. Chem. Soc.*, 1949, **71**, 1142) have reported a complete isotherm at 60° showing the four solid phases $Al_2(SO_4)_3,16H_2O$, $Al_2(SO_4)_3,9H_2O$, 1,3,12, and $Al_2(SO_4)_3$, the one succeeding the other as the acid concentration increased. Collet (*Compt. rend.*, 1950, **230**, 951) has reported the following sequence at 20° : the 18-, 16-, 10-, and 6-hydrates of the normal sulphate followed by 1,1,4; while Funaki (*Bull. Tokyo Inst. Tech.*, 1950, Series B, No. 1, 66) has claimed the sequence 18-, 16-, 9-hydrates followed by 1,5,0 at 25°. On the other hand, very careful work by Bassett and Goodwin (*J.*, 1949, 2239) has shown that at 25° up to an acid concentration of 47·5% only the 16-hydrate of the normal sulphate occurs as stable solid phase.

In an attempt to clarify this situation, a full investigation of the ternary system from 25° to 60° was undertaken and also of some features of the $Al_2(SO_4)_3$–H_2O system. Certain aspects of the corresponding ferric sulphate system have also been examined and a comparison of the two has helped to elucidate some features of the aluminium sulphate system. For the latter, it is of prime importance that the solubility determinations should be of the highest possible accuracy, for in assessing tie-line convergence points on the usual triangular diagram quite small errors assume major significance. This arises in view of the large molecular weight of aluminium sulphate compared with those of water and sulphuric acid. All techniques and analytical procedures were therefore the subject of special investigation.

TABLE 2. *Determination of* H_2SO_4 *in presence of* Al.

Taken : H_2SO_4, ml. 0·905N	$Al_2(SO_4)_3$, g.	Wt. ratio, $H_2SO_4 : Al_2(SO_4)_3$	Found : * NaOH ml. 0·481N
10·0	0·0	—	18·83
10·0	0·027	16	18·82
10·0	0·160	3	18·82
10·0	0·424	1	18·82

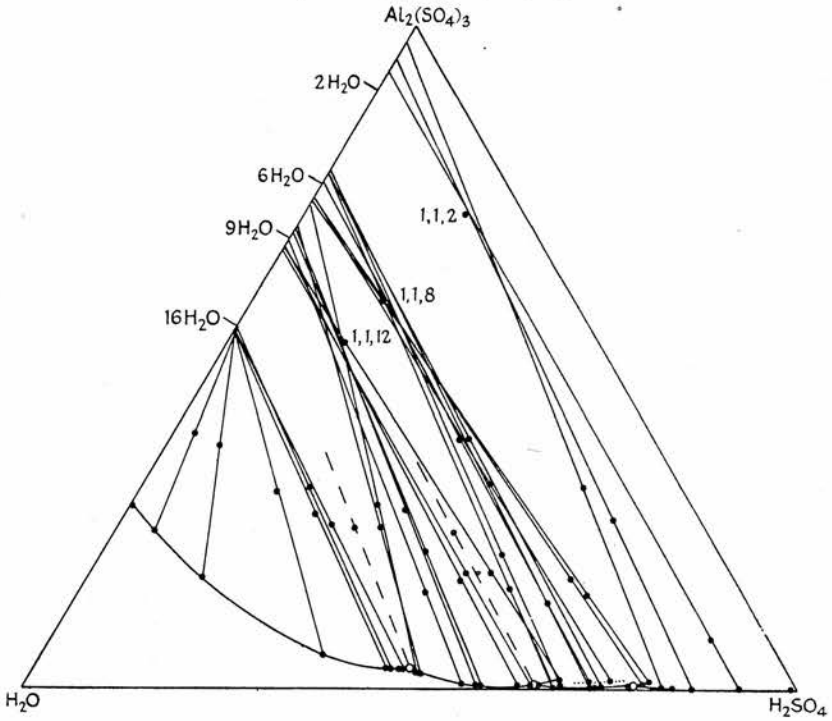
* Calc. : 18·82 ml.

H_2SO_4, ml. 0·905N	$Al_2(SO_4)_3$, g.	Wt. ratio, $H_2SO_4 : Al_2(SO_4)_3$	Found : † NaOH, ml. 0·0993N
1·00	0·0	—	9·12
1·00	0·25	0·17	9·15
1·00	0·85	0·05	9·12

† Calc. : 9·11 ml.

the complete neutralisation of the acid before addition of the fluoride was essential. A series of titrations was always carried out in which progressively larger amounts of alkali were added before the fluoride until no further increase in titre was observed. The results in Table 2 show this procedure to be reliable.

FIG. 1. *System* $Al_2(SO_4)_3$–H_2SO_4–H_2O *at* 25°.



Repeated comparison of the oxine–barium sulphate and volumetric methods for free acid determination showed that they agreed to 2 parts in 1000 except when both the free acid concentration and the acid : salt ratio were low. In this range, the volumetric method gave results up to 3% higher, and is considered more accurate for it gives the acid concentration directly instead of as a small difference between two large quantities both of which may contain an experimental error.

Ferric sulphate compounds were analysed for iron either by direct ignition with blowpipe heating to ferric oxide or by reduction with aluminium followed by permanganate titration (Cumming and Kay, *op. cit.*, p. 395). Total SO_4 radical was determined by titration at the boil with sodium hydroxide to phenolphthalein end-point.

Ternary Solubility Measurements.—Solubility determinations were carried out in a manner analogous to that given by Taylor (*loc. cit.*) with the addition that all initial solids by careful heating were brought completely into solution before being stirred to equilibrium. Certain mixtures at very high acid concentrations required the use of oleum in place of " AnalaR " sulphuric acid. The time to attain equilibrium varied from a few hours at the low-acid side to several months at the high-acid side of the system. Seeding with the desired solid phase was frequently advantageous, and occasionally after the desired solid phase had been obtained from a mixture of

known composition, the latter was adjusted to a different value by the addition of water or acid as required. Nevertheless, stubborn metastability was frequently encountered, particularly at high acid concentrations. At equilibrium, mixtures were filtered with suction either through a sintered-glass micro-filter stick of No. 3 porosity attached to a pre-heated pipette, or through a number 3 grade sintered-glass mercury filter suitably attached to a small receiver. The

TABLE 3. *The system* $Al_2(SO_4)_3$–H_2SO_4–H_2O.

Solution: $Al_2(SO_4)_3$, %	Solution: H_2SO_4, %	Moist solid phase: $Al_2(SO_4)_3$, %	Moist solid phase: H_2SO_4, %	Solid phase	Solution: $Al_2(SO_4)_3$, %	Solution: H_2SO_4, %	Moist solid phase: $Al_2(SO_4)_3$, %	Moist solid phase: H_2SO_4, %	Solid phase
				At 25°					
27·76	0·0	—	—	A	* 1·42	68·68	17·74	51·46	B
27·74	0·0	—	—	A	0·67	65·66	23·73	43·69	B + C
27·79	0·0	—	—	A	0·23	68·36	15·16	55·16	C
23·89	4·78	38·59	2·48	A	0·59	69·32	20·27	51·77	C
16·88	14·60	36·76	6·67	A	0·18	73·20	13·05	61·13	C
5·23	36·12	29·93	17·58	A	0·19	73·93	—	—	C
3·19	45·26	26·47	24·28	A	0·57	78·13	—	—	C
3·05	45·99	30·31	21·54	A	* 0·77	79·77	16·70	62·41	C
3·14	47·30	—	—	A	* 1·08	80·25	14·11	65·80	C
3·13	47·53	24·77	27·16	A	†† 0·6	78·5	—	—	C + E
3·22	48·30	24·33	30·50	A + B	** 1·12	72·61	37·85	37·26	D
2·50	49·55	27·98	31·61	B	* 0·36	74·60	—	—	D
2·46	50·10	24·28	33·81	B	* 0·37	74·60	37·98	38·50	D
0·95	56·21	14·73	44·54	B	** 1·31	75·33	30·97	44·65	D
0·75	58·10	27·11	35·74	B	0·18	82·49	30·39	57·00	E
0·62	58·89	20·78	41·43	B	0·12	83·90	—	—	E
0·56	63·48	16·32	48·33	B	0·14	86·48	25·72	63·17	E
0·64	65·32	17·50	48·44	B	† 0·01	92·71	7·62	85·09	E
* 0·68	66·20	—	—	B	<0·07	99·30	—	—	E
				At 30°.					
3·98	45·24	—	—	A	3·01	49·71	—	—	B
4·36	46·86	§ 51·25	14·12	A + B	0·93	57·89	38·35	26·75	B
4·06	47·50	—	—	B					
				At 50°.					
29·70	0·0	—	—	A	3·29	52·41	—	—	G
25·53	5·28	—	—	A	†† 3·30	53·90	—	—	G + B
20·57	13·22	—	—	A	* 3·81	52·53	—	—	B
11·67	31·27	—	—	A	* 3·48	53·61	—	—	B
10·02	36·41	—	—	A	3·27	54·20	—	—	B
* 9·91	39·65	34·87	17·64	A	2·27	59·03	—	—	B
* 9·90	40·36	—	—	A	* 2·22	61·31	—	—	B
†† 10·0	37·0	—	—	A + F	†† 2·20	60·00	—	—	B + C
8·93	39·40	—	—	F	0·77	64·90	—	—	C
†† 8·2	41·5	—	—	F + G	0·43	72·70	—	—	C
* 9·91	38·90	—	—	A + G	0·71	76·73	—	—	C
7·82	42·08	—	—	G	* 1·33	78·43	—	—	C
7·47	42·60	—	—	G	†† 0·80	77·00	—	—	C + E
6·16	44·94	—	—	G	0·07	83·00	—	—	E
5·61	46·26	49·23	14·40	G	<0·07	92·50	—	—	E
3·54	51·40	40·29	22·60	G					
				At 60°.					
* 14·82	31·56	—	—	A	* 12·44	36·95	—	—	G
* 14·43	33·91	—	—	A	* 11·44	38·39	—	—	G
†† 14·3	34·4	—	—	A + G	* 10·31	40·11	—	—	G
†† 17·0	25·5	—	—	A + F	* 9·21	42·09	—	—	G
12·56	32·80	—	—	F	6·76	46·61	—	—	G
10·18	37·45	—	—	F	†† 4·7	54·5	—	—	G + B
9·59	39·23	—	—	F	* 6·52	49·74	—	—	B
† 8·00	44·00	—	—	F + G	* 5·27	52·43	—	—	B
* 12·62	36·60	—	—	G	3·96	57·53	—	—	B

* = Metastable. ** = May be supersaturated. † = Al estimated colorimetrically with alizarin.
†† = Interpolated invariant points. § = Acetone-washed dry solids.

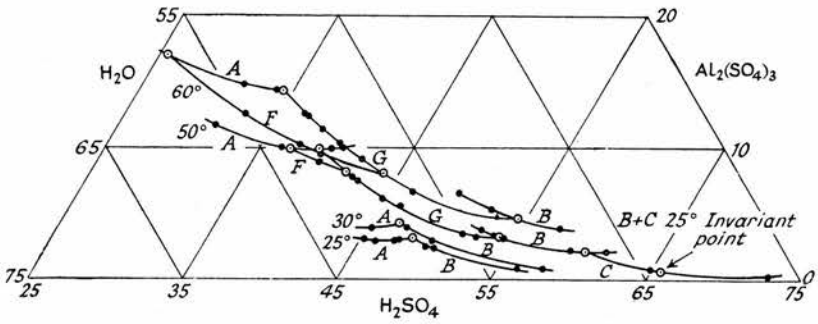
Solid phases:
A = $Al_2(SO_4)_3,16H_2O$.
B = $Al_2(SO_4)_3,H_2SO_4,12H_2O$
C = $Al_2(SO_4)_3,H_2SO_4,8H_2O$, stable form.
D = $Al_2(SO_4)_3,H_2SO_4,8H_2O$, metastable form.
E = " acidic " $Al_2(SO_4)_3,H_2SO_4,2H_2O$.
F = $Al_2(SO_4)_3,14H_2O$.
G = $2Al_2(SO_4)_3,H_2SO_4,24H_2O$.

Further details are given on pp. —

open end of the mercury filter could be closed with a calcium chloride tube, and the whole unit immersed in the thermostat so that the very slow filtering mixtures encountered at the high acid side of the system could be filtered without disturbance of the equilibrium. After filtration, weighed samples of the solution and moist solids were diluted to a standard volume and analysed. Continuous use was made of microscopical examinations and of *X*-ray powder photographs in recognising solid phases and invariant points and particularly in following the course of solid phase transitions. Results are given in Table 3 and Figs. 1 and 2. The position of all tie-lines was determined with the aid of mathematical extrapolation to eliminate drawing errors. Compositions are by weight.

Indicator Experiments in the Ternary System.—Three indicators were used: radioactive cæsium sulphate, manganese sulphate, and hydrogen chloride. Details for the radioactive tracer work at 30° have been given elsewhere (Taylor and Scott, *loc. cit.*), and the manganese (one drop of 30% sulphate solution per 50 g. of ternary mixture) was used in essentially the same manner at 25°, the indicator being determined colorimetrically as permanganate after oxidation with potassium periodate in presence of phosphoric acid (Cumming and Kay, *op. cit.*, p. 270). It was essential to add the manganese sulphate after the ternary mixture had been brought to equilibrium, otherwise the manganese was completely co-precipitated with the solid phase. In

FIG. 2. *System* $Al_2(SO_4)_3$–H_2SO_4–H_2O at 25°, 30°, 50°, *and* 60°



Solid phases indicated by capital letter as in Table 3.
Open circles denote isothermal invariant points.

addition to experiments on acidic solid phases, a test of the whole procedure was carried out with a mixture known to contain $Al_2(SO_4)_3,16H_2O$ as solid phase, the free acid concentration being about 46%, *i.e.*, as high as conveniently possible without causing the solid to be transformed into 1,1,12. Experiments at very high acid concentrations were unsuccessful owing partly to precipitation of the indicator and partly to its adsorption on the very finely divided solid phases occurring at such acid concentrations. In the case of hydrogen chloride at 25°, the indicator was added at the outset and determined after equilibrium was reached by electrometric titration with N/100-silver nitrate. The presence of aluminium and sulphate was shown not to influence the chloride determination. The use of hydrogen chloride was limited by its low solubility in concentrated sulphuric acid solutions at atmospheric pressure. Results are given in Table 4.

TABLE 4. *Indicator experiments.*

			Composition: Calc.:		Found:	
Indicator	Temp.	Solid phase	$Al_2(SO_4)_3$, %	H_2SO_4, %	$Al_2(SO_4)_3$, %	H_2SO_4, %
$MnSO_4$	25°	A	54·3	0·0	58·4	−3·7
Cs_2SO_4	30	B	52·1	14·9	51·3	15·9
$MnSO_4$	25	B	52·1	14·9	51·5	15·1
HCl	25	B	52·1	14·9	48·1	17·8
$MnSO_4$	25	D	58·5	16·8	55·5	21·6

Solid phases as in Table 3.

Pure Dry Solid Phases.—Samples of all the solid phases listed in Table 3, together with several others not directly encountered in the solubility work, were prepared and analysed, and *X*-ray powder photographs were taken with a Unicam 9-cm. camera. A number of similar ferric compounds, whose compositions have been reliably established by Posnjak and Merwin (*J. Amer.*

Chem. Soc., 1922, **44**, 1965), were also prepared and examined for isomorphism with corresponding aluminium compounds. In cases involving the separation of a solid from a mother-liquor the simple procedure was adopted of washing the moist solids thoroughly with " AnalaR " acetone containing 1% of water, followed by drying at room temperature in a current of dry air and finally for five minutes at a pressure of less than 1 mm. of mercury. Microscopical appearances are recorded below, compositions in Table 5, and lattice spacings in the Appendix.

$Al_2(SO_4)_3,16H_2O$ (*A in Tables* 3, 4 *and* 5). As a test of the washing procedure in removing acidic liquid, the hydrate was separated at 25° from a saturated mother-liquor containing approximately 46% of free acid. The resulting dry solid contained 16·2 molecules of water of crystallisation and zero free acid. When grown very slowly from dilute solution, the hydrate was obtained as extremely thin elongated hexagons with vertical angle 92° 40′ (cf. Delacharlonny, *Compt. rend.*, 1883, **96**, 844) and symmetrical extinction, but in solubility experiments the usual habit was long thin laths extinguishing at an angle of about 43° with the length. The lattice spacings corresponded exactly with those given by Bassett and Goodwin (*loc. cit.*).

$Al_2(SO_4)_3,14H_2O$ (*F in Tables* 3 *and* 5). This hydrate was obtained only from solubility experiments at 50° and 60°, and was formed always as the result of a very slow transformation of either the 16-hydrate or the 2,1,24 phase. Its precipitation from solutions metastable with respect to 2,1,24 was sometimes assisted by addition of a little water. Washing was with warm acetone, the resulting solid containing only a trace of free acid. The crystals occurred as long narrow laths with a single oblique end-face, some showing parallel extinction and some not. It was distinguished from the 16-hydrate most reliably either by analysis of the dry solid or by its *X*-ray powder photograph.

$Al_2(SO_4)_3,9H_2O$. Recrystallised 16-hydrate was dried in air at 100° till it contained 8·7 molecules of water of crystallisation and then heated in a small sealed Pyrex tube at 160° for 9 weeks, during which time the solid underwent a visible recrystallisation. *X*-Ray powder photographs showed that the solid was practically structureless before heating but gave a characteristic diagram afterwards, such that the crystals obtained are thought to be essentially the 9-hydrate. They were highly birefringent, biaxial positive, with irregular shapes.

$Al_2(SO_4)_3,6H_2O$. This was prepared in the same way as the 9 hydrate starting from an amorphous solid containing 6·7 molecules of water of crystallisation. Small birefringent needles with oblique extinction were obtained which gave a good *X*-ray diagram.

Anhydrous $Al_2(SO_4)_3$. Heating of recrystallised 16-hydrate in air at 500° for 150 hours gave a product which analysis showed to be $Al_2(SO_4)_3$ apart from a slight loss of SO_3 and a very little residual water. The *X*-ray diagram showed the product to be well crystallised.

" *Acidic*" *anhydrous* $Al_2(SO_4)_3$. By dissolving 3 g. of " AnalaR " salt in 25 ml. of 70—80% acid and gently boiling the solution till fuming occurred, small thin hexagonal plates were first precipitated (see below under 1,1,2), which on further heating were transformed into dense birefringent small square tablets (*d* 2·7). Although the *X*-ray diagram was identical with that of anhydrous $Al_2(SO_4)_3$, the square tablets contained about 1% of water and 7% of free acid. The presence of the latter on the surface of the crystals would indicate failure of the acetone washing procedure but this was shown not to be the case as follows. After immersion of the tablets in distilled water with intermittent stirring for 10 minutes and filtering, the filtrate contained only 15% of the free acid present in the crystals and a small quantity of aluminium ion. Furthermore, although the excess of acid varied a little from one preparation to another, yet it was independent of the volume of wash liquid.

$2Al_2(SO_4)_3,H_2SO_4,24H_2O$ (*G in Tables* 3 *and* 5). This phase was obtained as well-formed 0·5-mm. six-sided plates, biaxial negative, in solubility experiments at 50° and 60° by slow transformation of previously precipitated 16-hydrate or 1,1,12, and over appreciable ranges remained metastable with respect to the 14-hydrate for long periods. Whether it was isolated by acetone or by absolute alcohol washing, the composition was the same and the dry crystals appeared completely unchanged. Although the two tie-lines could indicate a composition of 2,1,22, analyses for three different preparations were very close to the composition 2,1,24, and the latter is therefore preferred.

$Al_2(SO_4)_3,H_2SO_4,12H_2O$ (*B in Tables* 3, 4, *and* 5). Crystals of this composition were obtained very easily at all temperatures in the solubility work. The habit was small, very thin, birefringent plates, almost square, many of which had one or both pairs of opposite corners truncated.

$Al_2(SO_4)_3,H_2SO_4,8H_2O$, *Stable form* (*C in Tables* 3 *and* 5). Several days' stirring were required even with seeding to induce precipitation of this solid as extremely small birefringent needles.

$Al_2(SO_4)_3,H_2SO_4,8H_2O$, *Metastable form* (*D in Tables* 3, 4, *and* 5). At 25° in the middle of the 1,1,8 range, a metastable form was obtained in quantity provided the solution initially was

highly supersaturated; from less supersaturated solutions both forms frequently appeared together. The crystals were in the form of rectangular blocks with bevelled end-faces, biaxial positive, a habit which was completely unchanged after acetone washing. The composition of different preparations varied slightly, having 1—2% of acid in excess of the composition 1,1,8. Doubling the quantity of wash liquid did not alter the composition. The crystals proved too unstable in air to give a reliable *X*-ray diagram, but a photograph of a mush of crystals and mother-liquor gave sufficient spacings to show that the two forms probably had different structures.

$Al_2(SO_4)_3,H_2SO_4,2H_2O$. The hexagonal plates referred to on p. in the preparation of "acidic" anhydrous $Al_2(SO_4)_3$ gave analyses very close to the composition 1,1,2. The hexagons were regular and isotropic normal to the six-fold axis, and the crystals thus belong to the hexagonal class. Observations during six months showed that transition to the square tablets phase did not occur below about 200°.

"*Acidic*" $Al_2(SO_4)_3,H_2SO_4,2H_2O$ (*E in Tables* 3 *and* 5). From supersaturated solutions containing more than 80% of free acid, small, roughly spherical, random aggregates of birefringent crystals were precipitated on prolonged stirring. Although these aggregates contained several units % more sulphuric acid and water (quantities which varied slightly from one preparation to another) than 1,1,2, the *X*-ray powder photographs were very similar, showing that both substances had essentially the same lattice structure. The composition was not dependent on the volume of wash-liquid used.

TABLE 5. *Dry solid phases.*

Temp. of preptn.	Solid phase	Composition: Calc.: $Al_2(SO_4)_3$, %	H_2SO_4, %	Found: $Al_2(SO_4)_3$, %	H_2SO_4, %
Aluminium sulphate compounds.					
25°	A	54·3	0·0	53·16	0·0
				53·41	0·0
				54·00	0·0
60	F	57·57	0·0	58·23	<0·2
				58·29	<0·1
				57·20	<0·1
25	B	52·1	14·94	51·45	15·02
50	B	52·1	14·94	51·29	15·36
				51·41	15·14
50	G	56·30	8·07	56·51	8·63
				56·47	8·48
				56·20	8·39
25	C	58·50	16·78	57·24	18·01
50	C	58·50	16·78	58·19	17·42
25	D	58·50	16·78	57·35	17·91
				56·20	18·84
				56·36	18·92
25	E	71·9	20·6	63·97	23·28
				64·85	23·20
				64·80	22·29
50	E	71·9	20·6	67·20	24·08
~190	1,1,2	71·9	20·6	71·15	20·38
~300	"Acidic" anhyd.	100·0	0·0	91·31	7·88
				93·27	5·87
500	Anhydrous	100·0	0·0	100·9	−2·57

Solid phases as in Table 3.

		$Fe_2(SO_4)_3$, %	H_2SO_4, %	$Fe_2(SO_4)_3$, %	H_2SO_4, %
Ferric sulphate compounds.					
25	8-Hydrate	73·52	0·0	73·0	0·08
25	1,1,8	62·27	15·28	62·6	14·5
50	1,1,2	74·87	18·36	74·4	17·67
~300	Anhydrous	100·0	0·0	99·98	0·0

Alunite. About 2% of the 9-hydrate preparation was very slow to dissolve in boiling dilute sulphuric acid. This residue, after-being washed with water and dried (P_2O_5) in a desiccator, was found to have an *X*-ray powder photograph characteristic of the alunite group. It contained only Al and SO_4 apart from water and may therefore have the composition $H_2O[Al_3(OH)_5H_2O](SO_4)_2$, which is one member of the alunite series (Bassett and Goodwin, *loc. cit.*; Bassett, *J.*, 1950, 1460).

Coquimbite. A Royal Scottish Museum specimen, number 1875/9/9, was made available

through the kind co-operation of Dr. C. D. Waterston. With assistance from Mr. A. R. Chalmers, the mineral was shown to have the composition $Fe_{1\cdot54}Al_{0\cdot46}(SO_4)_3,9H_2O$.

$Fe_2(SO_4)_3,8H_2O$. From a saturated solution containing 2—3% of free acid, after partial evaporation over phosphoric oxide followed by several days' stirring at 25°, minute fawn needles were obtained. After filtration, the hydrate was washed with a few drops of ice-cold water and then with acetone. It was found that transition to the 1,1,8 compound commenced in solution at a free acid concentration of about 5%, which is contrary to the published data (collected refs. in Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Van Nostrand, 3rd edn., 1940).

TABLE 6. *The system* $Al_2(SO_4)_3$–H_2O [solid phase: $Al_2(SO_4)_3,16H_2O$].

Temp., °c	50·5	73·4	75·0	76·7	82·0	88·0	95·1	99·2	103·2	110·4	112·2
Solution · $Al_2(SO_4)_3$, %	30·09	33·33	33·63	34·28	36·60	38·74	41·86	43·90	46·85	52·0	53·0

$Fe_2(SO_4)_3,H_2SO_4,8H_2O$. Baskerville and Cameron's phase equilibria data (*J. Phys. Chem.*, 1935, **39**, 769) being used, pale fawn six-sided plates were obtained at 25°. They were biaxial with the acute bisectrix almost perpendicular to the plane of the crystal.

$Fe_2(SO_4)_3,H_2SO_4,2H_2O$. Very irregular fawn birefringent plates were obtained at 50°, Posnjak and Merwin's phase data (*loc. cit.*) being used.

Anhydrous $Fe_2(SO_4)_3$. Pale fawn, square and rectangular tablets, some with extra faces, were obtained by boiling 2 g. of B.D.H. ferric sulphate in 20 ml. of 80% acid till the mixture fumed very strongly. The anhydrous compound was found to be the only equilibrium solid phase under such conditions (cf. Posnjak and Merwin, *loc. cit.*).

$(NH_4)_2SO_4,Fe_2(SO_4)_3$. This was prepared as well-formed nearly colourless hexagonal plates by low-temperature dehydration of ferric alum, and its composition checked by analysis.

$(NH_4)_2SO_4,Fe_2(SO_4)_3,4H_2O$. This was obtained as pale violet, tetragonal bipyramids by crystallisation at 25—30° of a solution of ferric alum strongly acidified with sulphuric acid. This *compound* does not appear to have been recorded previously [Found: Fe_2O_3, 26·4; $(NH_4)_2O$, 8·7; SO_3, 52·7. $(NH_4)_2SO_4,Fe_2(SO_4)_3,4H_2O$ requires Fe_2O_3, 26·4; $(NH_4)_2O$, 8·6; SO_3, 53·0%. The mother-liquor contained 4·5, 1·6, and 33·4%, respectively].

With the exception of the metastable aluminium 1,1,8 compound which dissolved readily, all solid phases with 9 or less molecules of water of crystallisation dissolved in water extremely slowly. Coquimbite and $Fe_2(SO_4)_3,8H_2O$ hydrolysed in water with the formation of a brown precipitate, but dissolved readily and completely in dilute acid.

Some Features of the $Al_2(SO_4)_3$–H_2O *System.*—(1) In a search for lower hydrates, solubility experiments by the synthetic method (cf. Taylor and Vincent, *J.*, 1952, 3218) were carried out in sealed tubes. Up to 112·2° (Table 6) the solid phase was the 16-hydrate and this probably just fails to have a congruent m. p. Above 112° two different solid phases appeared, but results were so erratic owing to the extreme slowness with which equilibrium was established in the highly viscous solutions that no estimate of the composition of the new phases could be made. At a composition corresponding to the 12-hydrate, the temperature of complete solution was about 200°. Since the 16-hydrate is only just able to give a congruent solution at 25°, and since hydrolysis may be expected to increase with rising temperature, some of the solutions in Table 6 may have been metastable with respect to a basic salt.

(2) At 25°, measurement of dissociation pressures, a McBain–Bakr silica spring balance and mercury manometer in an all-glass vacuum system being used, confirmed (*a*) the occurrence of the 14-hydrate, and (*b*) the ability of the 16-hydrate to absorb up to 0·8 molecule of water without the appearance of a liquid phase. The dissociation pressure for the reaction 16-hydrate $\rightleftharpoons$ 14-hydrate + $2H_2O$ was 10·5 mm. of mercury, and the vapour pressure of saturated aluminium sulphate solution 21·3 mm. For hydrates containing less than 14 molecules of water, dissociation pressures are less than 3 mm.

(3) Orthobaric dehydration of the 16-hydrate in air saturated at 25° with water vapour (cf. Milligan and Weiser, *J. Phys. Chem.*, 1934, **38**, 513) confirmed the observations made in (2) above, but gave no information regarding hydrates lower than 14 owing to the prohibitive time to reach equilibrium.

DISCUSSION

The stable solid phase up to moderate acid concentrations in the 25—60° range is normal aluminium sulphate containing between 16 and 17 molecules of water of crystallisation. This phase is best regarded as a true 16-hydrate with the extra approximate 0·5

H_2O held by adsorption or in a zeolitic manner because (*a*) there is no evidence from any section of the work for a 16·5 $\longrightarrow$ 16-hydrate transition, and (*b*) the system solid 16-hydrate–water vapour was observed to be univariant over the composition range from 16 to 16·8 molecules of water per molecule of aluminium sulphate in the isothermal and orthobaric dehydration experiments. As far as tie-lines are concerned, the extra water is indistinguishable from true water of crystallisation and may therefore be held by relatively strong forces. This view is further supported by the facts that the extra water is invariably present in the solid no matter what its source, and the hydrate is not efflorescent in air.

In spite of the attention given to all analytical procedures, Fig. 1 shows that, with the exception of the 16-hydrate, the tie-line information, although clearly differentiating one solid phase from another, gave little more than suggestions as to their composition : following the 16-hydrate, a succession of highly hydrated acidic phases was favoured, but a sequence of lower hydrates of the normal sulphate was not ruled out. Recourse was therefore made to (1) indicator experiments, (2) isolation and analysis of dry solid phases, and (3) establishment by *X*-ray methods of isomorphism with corresponding ferric compounds of known composition.

The severe conditions which the ideal indicator in phase equilibria work must fulfil have been outlined by Taylor and Scott (*loc. cit.*), and it is seldom that such experiments yield more than suggestions as to solid-phase compositions. The unusual success with radioactive cæsium sulphate and manganese sulphate was due to both the minute quantity required and the accuracy with which they could be detected. Their use showed very definitely (Table 4) that phase B had the composition 1,1,12. The result for the hydrogen chloride indicator was less definite, but even so the acidic nature of the solid phase was clearly suggested. For the metastable phase D, manganese being used as indicator, the preferred composition was again that of 1,1 acidic solid. The fact that an experiment on the 16-hydrate with manganese as indicator definitely showed the absence of free acid from the solid phase, confirmed that the indicator procedure was trustworthy.

In the absence of radioactive indicator experiments at high acid concentrations, and the failure of the manganese and hydrogen chloride indicators under such conditions, attempts were made by washing with acetone to isolate all the solid phases including the ferric compounds in the dry state for analysis. Such a procedure involves the possibility of (*a*) decomposition by loss or gain of water, acid or solvent, and (*b*) precipitation of unwanted solids from the mother-liquor. Point (*a*) is considered unimportant since (1) both the 16-hydrate and the 1,1,12 phase after isolation had compositions very close to those required by their formulæ, (2) the crystal habit of several of the phases appeared unchanged after the washing procedure, and (3) compositions were independent of the volume of wash liquid used. Furthermore, a number of the phases in Table 5 have to within close limits stoicheiometric compositions, and this would have been most unlikely if significant decomposition had occurred. Point (*b*) was eliminated by the fact that addition of acetone to the mother-liquors in the proportions used in the washing procedure gave no precipitates in the time interval required to complete the washing. For these reasons, the compositions assigned to the solid phases in Tables 3, 4, and 5 are believed correct. The nature of the three phases D, E, and "acidic" anhydrous $Al_2(SO_4)_3$, whose compositions were not truly stoicheiometric, will be discussed below.

Further confirmation of the acidic nature of the solid phases was obtained by comparison of the *X*-ray powder photographs of corresponding aluminium and ferric compounds. In making these and subsequent comparisons, it was essential to compare the actual photographic films and not sets of calculated lattice spacings, for with the latter, important similarities and differences could be overlooked. In the case of the 1,1,8 compounds, the photographs were practically identical, showing that the two solids were isomorphous and therefore had the same atomic composition. For the 1,1,2 and anhydrous pairs of compounds, the photographs were sufficiently similar to indicate distinct possibilities of isomorphism. It is noteworthy that the characteristic features of the photographs of the 1,1,2 pair were also found in $(NH_4)_2SO_4,Fe_2(SO_4)_3$, showing that the oxonium ion may be replaced isomorphously by the ammonium ion (cf. Shiskin, *Zhur. Obs. Khim.*, 1951, **21**, 456; *Chem. Abs.*, 1951, **45**, 6115). Lattice dimensions and space-groups already known

for $K_2SO_4,Al_2(SO_4)_3$, $(NH_4)_2SO_4,Al_2(SO_4)_3$, and $(NH_4)_2SO_4,Fe_2(SO_4)_3$ ("Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., 31st edn., 1949, p. 2056, 2062) show that these also are isomorphous and belong to the hexagonal class as does the aluminium 1,1,2 compound. This is convincing evidence that the last compound (*a*) has the composition denoted by 1,1,2, (*b*) is an oxonium salt, and (*c*) is not the dihydrate of the normal sulphate. The *X*-ray diagram of $(NH_4)_2SO_4,Fe_2(SO_4)_3,4H_2O$ showed no resemblance to any of the other compounds dealt with in this paper.

In the case of coquimbite and the 9-hydrate of aluminium sulphate, less resemblance could be traced between the photographs than was expected, for it is well known that up to 50% of the iron in coquimbite can be replaced by aluminium. The lack of resemblance may cast doubt on the nature of the aluminium compound, but on the other hand it is known that coquimbite, and probably therefore the corresponding aluminium compound also, is polymorphous, and since the aluminium compound was prepared at 160°, the photographs may be those of structurally unrelated polymorphs.

The determination of numerous invariant points, either directly or by extrapolation of solubility curves (Table 3), allowed the direction of the univariant lines for the transitions 16-hydrate $\longrightarrow$ 1,1,12, 16-hydrate $\longrightarrow$ 2,1,24, and 1,1,12 $\longrightarrow$ 1,1,8 to be fixed on the polythermal projection diagram with certainty, so the empirical criteria suggested by Taylor (*loc. cit.*) for distinguishing between normal and acid sulphates could be applied. According to these criteria, for the first two transitions where an increase in acid content occurs in the direction from left to right, points on the univariant lines would be expected to show an increase in sulphuric acid concentration with rising temperature, while for the third transition, where dehydration occurs from left to right, an increase in water concentration could be expected. It should be noted that the first two transitions also involve dehydration from left to right, and depending on whether the hydrate or acid sulphate characteristics of the phases on the right-hand side are predominant, the direction of the univariant lines may follow either the water of the acid criteria respectively. In fact, all three transitions do conform to the hydrate–lower hydrate case, and it may therefore be that the hydrate nature of the phases is the more important, a view which is not unreasonable in view of their high degree of hydration. Owing to very stubborn metastability, invariant points and univariant lines for the transitions 16-hydrate $\longrightarrow$ 14-hydrate, 14-hydrate $\longrightarrow$ 2,1,24, and 2,1,24 $\longrightarrow$ 1,1,12 were obtained only by considerable extrapolation of solubility curves and are therefore less reliable. Nevertheless, Fig. 2 suggests that the first transition does conform to the hydrate–lower hydrate case, and the second and third to the hydrate–acid sulphate criterion. According to Posnjak and Merwin's data (*loc. cit.*), transitions which involve simultaneously dehydration and an increase in the acid content of the solid phases do not occur in the corresponding ferric sulphate system; all transitions conform without ambiguity to Taylor's criteria although the position is complicated by retrograde solubility.

The nature of the non-stoicheiometric solid phases can be considered as follows. Since the *X*-ray powder photograph of "acidic" anhydrous $Al_2(SO_4)_3$ was identical even in the high-order lines with that of the true anhydrous salt, the two must have the same lattice structure. Since the extra acid and water in the former were present in roughly the same proportions as in the mother-liquor and were shown to be contained within the crystals and not on the surface, the presence of inter-crystallite liquid is indicated. The relationship between the 1,1,2 and the "acidic" 1,1,2 phase is not so simple, for although the powder photographs showed that they were both essentially the same chemical individual, yet the absence from the "acidic" 1,1,2 photograph of two or three of the low-order lines of moderate intensity pointed to slight differences in lattice structure. The latter, it is suggested, may be the result of lattice defects caused by the occasional absence of an aluminium ion, electrical neutrality being preserved by the substitution of three hydrogen ions in its place. The "holes" would be distributed on a statistical basis and the hydrogen ions would be associated with oxygen atoms of $SO_4^=$ ions. Such a substitution process would be analogous to that known to occur in the alunite series (Bassett and Goodwin, *loc. cit.*), and would result in the "acidic" phase's varying slightly in composition from one preparation to another, as was in fact observed. The substitution on the average of one

aluminium ion in every 16 transforms the composition 1,1,2 into 1,1·27,2·14 which would account very well for the acid concentration of the " acidic " phase. The latter's water content however varied between 2·46 and 3·68 molecules, which suggests that inclusion of acidic liquid had occurred in addition to a degree of substitution less than one in 16. Considering the habit of the " acidic " phase, inclusion of liquid would be very probable. Since the points representing the dry solid lay significantly on the water side of the corresponding group of tie-lines, absorption of a small quantity of liquid richer in water than the mother-liquor may have occurred during the washing procedure. Comparison of powder photographs showed that other transformations such as 9-hydrate $\longrightarrow$ 1,1,12 and 6-hydrate $\longrightarrow$ 1,1,8, caused by the substitution of one aluminium ion in every four, had not occurred. In view of the composition, tie-line and indicator experiment data for the metastable phase D, the latter is best regarded as a second form of the 1,1,8 compound. The *X*-ray data showed that the structures of the two forms were probably unrelated, and the extra sulphuric acid in the metastable form may therefore arise from occluded liquid.

The divergence of opinion of previous authors regarding the nature of the solid phases is probably due to the two factors : (*a*) too great reliance being placed on apparent tie-line convergence and (*b*) the existence of metastable equilibria. For example, it would be difficult on the basis of tie-line data alone to distinguish with certainty between the solid phases 1,1,8, 1,2,10, and 1,3,12, and although Henry and King (*loc. cit.*) have reported the solid 1,3,12, their description of the phase corresponds almost exactly with the stable form of our 1,1,8 substance. Similar difficulties apply to the two trios 9-hydrate–1,1,12–2,1,24 and anhydrous–dihydrate–1,1,2. Henry and King also report at 60°, following the acidic 1,3,12 (or more probably 1,1,8) with increasing acid concentration, the surprising appearance of the anhydrous normal sulphate. This phase may, as mentioned above, have been mistaken for the 1,1,2 compound, or their solutions may have been metastable with respect to 1,1,2, for we have observed the " acidic " anhydrous phase (prepared separately) to persist with the " acidic " 1,1,2 phase in contact with saturated solution (*ca.* 80% of free acid) for twelve months at 25—60° without showing any signs of approach to true equilibrium. On the other hand, we have never observed the formation of the " acidic " anhydrous phase in solution below about 200°.

Appendix

The *X*-ray photographs were taken with a 9-cm. camera, Cu-$K\alpha$ radiation being used for the aluminium compounds, and Co-$K\alpha$ for the ferric compounds. Only the first 10—15 lines are recorded, though many more were visible in different cases. Intensities were estimated visually; s signifies strong, m moderate, w weak. In Table 7, the spacings *d* are given in Ångström units. The spacings for $Fe_2(SO_4)_3,H_2SO_4,8H_2O$ agree with, but are more complete than, those given by Amiel, Gourdonneau, and Vauthier (*Compt. rend.*, 1945, **220**, 402). Their results for $Fe_2(SO_4)_3,9H_2O$, prepared by Recoura's method (*Ann. Chim. Phys.*, 1907, **11**, 264), differ appreciably from those given below for $Al_2(SO_4)_3,9H_2O$ or coquimbite.

Table 7. *Lattice spacings.*

$Al_2(SO_4)_3,14H_2O$		$Al_2(SO_4)_3,9H_2O$		$Al_2(SO_4)_3,6H_2O$		$Al_2(SO_4)_3$		Alunite		Al, 1,1,12	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
7·37	w	7·56	m	7·74	w	5·72	m	4·95	m	8·28	w
5·62	w	5·50	w	6·70	m	4·19	m	3·57	w	7·40	w
5·15	w	4·64	s	5·58	w	3·47	s	3·01	s	6·12	w
4·55	s	4·26	s	4·73	s	2·88	m	2·79	w	4·74	m
4·26	m	3·80	s	4·03	w	2·63	m	2·25	m	4·32	s
3·91	m	3·48	s	3·80	m	2·58	m	1·91	m	4·08	m
3·63	m	3·14	m	3·59	m	2·33	w	1·87	w	3·86	w
3·29	w	2·98	m	3·29	m	2·29	w	1·75	m	3·68	m
2·98	w	2·71	m	3·01	m	2·19	m	1·65	w	3·55	w
2·78	w	2·64	w	2·67	w	2·02	m	1·55	w	3·27	w
2·66	w					1·98	w	1·48	w	3·14	w
2·59	w					1·92	m	1·46	m	2·99	m
2·53	w									2·80	m
										2·66	w
										2·56	m

TABLE 7.—*continued.*

Al, 1,1,8, stable		Al, 1,1,8, metastable		Al, "acidic," 1,1,2		Al, 1,1,2		Coquimbite		$Fe_2(SO_4)_3,8H_2O$	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
9·40	s	6·27	w	8·28	m	10·48	s	9·63	w	10·54	m
8·96	s	5·19	w	4·06	m	7·82	m	8·58	s	7·23	w
5·12	w	4·68	s	3·93	m	4·04	w	5·53	m	6·87	s
4·68	s	4·16	w	3·74	w	3·86	m	4·65	m	5·26	w
4·40	w	3·97	w	3·40	s	3·70	m	3·64	m	4·84	w
3·99	m	3·89	w	3·14	w	3·57	m	3·49	w	4·45	m
3·65	w	3·74	m	2·90	w	3·34	s	3·36	m	4·22	w
3·46	m	3·61	m	2·64	m	3·09	w	3·03	w	4·01	w
3·26	m	3·48	m	2·37	m	2·95	w	2·77	s	3·58	m
3·04	s	3·14	w	2·26	m	2·85	w	2·54	w	3·35	w
2·69	w	2·99	w	2·03	w	2·73	w	2·31	w	3·22	w
2·66	w	2·89	w	1·94	w	2·58	m				
2·59	w	2·80	w			2·35	m				
2·56	w	2·76	w			2·31	w				
2·49	w	2·61	w			2·26	m				

Fe, 1,1,8		Fe, 1,1,2		$Fe_2(SO_4)_3$		$(NH_4)_2SO_4,Fe_2(SO_4)_3$		$(NH_4)_2SO_4,Fe_2(SO_4)_3,4H_2O$	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
9·22	s	10·28	m	6·08	m	8·10	s	6·91	w
8·81	s	9·01	m	5·32	w	4·49	w	5·77	s
5·19	w	7·72	m	4·40	m	4·10	w	5·15	w
4·79	w	4·05	w	4·14	m	3·67	w	4·55	w
4·68	m	3·90	w	3·71	w	3·41	m	3·80	s
4·18	w	3·71	w	3·59	s	2·69	w	3·27	s
4·01	m	3·59	w	3·26	w	2·39	m	2·88	w
3·50	m	3·35	s	3·16	w	2·07	w	2·77	w
3·26	m	3·26	w	2·99	m	1·96	w	2·67	w
3·08	m	3·08	w	2·90	w				
2·75	w	2·57	w	2·74	m				
2·64	w	2·39	m	2·69	w				
2·57	w	2·27	w	2·63	w				
2·49	w	2·02	w	2·42	w				

Grateful acknowledgments are made to Imperial Chemical Industries Limited and the Moray Endowment Fund for grants for chemicals and apparatus. Part of this work was carried out during the tenure of an I.C.I. Fellowship (by D. T.).

UNIVERSITY OF EDINBURGH.

[*Received, July 18th,* 1952.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

Preprinted from the Journal of the Chemical Society,
August 1953, (510), pages 2502—2503.

510. *The System* $Cr_2(SO_4)_3$–H_2SO_4–H_2O.

By Duncan Taylor.

In the system $Al_2(SO_4)_3$–H_2SO_4–H_2O, Taylor and Bassett (*J.*, 1952, 4431) have shown that, (*a*) as the acid concentration increases at 25° the solid phase $Al_2(SO_4)_3,16H_2O$ is followed by an unusual series of hydrated acid sulphates, (*b*) the 14-hydrate appears as a stable solid phase only at higher temperatures (50—60°), and (*c*) the anhydrous sulphate is not obtained except in concentrated acid solutions near the boiling point. In view of the well-known isomorphism of aluminium and chromic compounds, it was of interest to see if the same behaviour was observed in the corresponding chromic sulphate system, especially since in the latter there is a much stronger tendency for the formaton of complex co-ordination compounds. Furthermore, although extensive data are available regarding hydrated and acid sulphates of chromium (Mellor, " Inorganic and Theoretical Chemistry," Longmans, 1924, Vol. 11, p. 434), no systematic investigation of the ternary system appears to have been published previously.

From our work it is concluded that (*a*) chromium does not form a series of hydrated acid sulphates as does aluminium, and (*b*) many of the data in Mellor (*op. cit.*) regarding acid sulphates of chromium are unreliable.

Experimental.—Phase-equilibria data were obtained at 25° by using techniques very similar to those already described for the aluminium sulphate system, except that to obtain dry samples of the solid phases the wash liquid was methanol at low sulphuric acid concentrations and acetone containing 10% by volume of methanol at high acid concentrations. These wash-liquids caused no dissolution of the solid phases and no precipitation of solids from the appropriate saturated solutions. Several months' stirring were used in all cases to establish solid–liquid equilibrium. This was essential because it was frequently observed, particularly at low acid concentrations, that a solid phase may be precipitated but redissolved within a few days as the nature of the chromium co-ordination in the liquid phase changed.

Chromic sulphate (B.D.H.) was used as starting material without further purification; it was shown to contain slightly more than 16 molecules of water of crystallisation and had an *X*-ray powder photograph identical with that of solid A (see Table). Other reagents were " AnalaR " wherever possible.

Analytical procedure. All samples of liquid and solid phases, except the anhydrous sulphate, were analysed for total sulphate and chromium, water being determined by difference. Experiments with synthetic mixtures showed that total sulphate could be determined with an accuracy of a few parts in 1000 (low tendency rather than high) by titration with sodium hydroxide to a first end-point in the cold with phenolphthalein as indicator and then completing the titration at the b. p. These results were irrespective of the ratio $Cr_2(SO_4)_3 : H_2SO_4$ and of the total weight of chromium present. Chromium was determined by oxidation to the dichromate stage with ammonium persulphate (Vogel, " Quantitative Inorganic Analysis," Longmans Green & Co., 1948, p. 370). Anhydrous chromic sulphate could not be dissolved in water except in presence of chromous ions (cf. Sidgwick, " Chemical Elements and Their Compounds," Oxford, 1950, Vol. 2, p. 1013), and was analysed only for chromium by ignition to Cr_2O_3. Since the anhydrous phase was formed in boiling concentrated sulphuric acid, its water content was assumed to be less than 1·0% [cf. anhydrous $Al_2(SO_4)_3$].

Results. Analyses for all liquid and solid phases are given in the Table in compositions by weight. At 25° up to an acid concentration of about 10%, $Cr_2(SO_4)_3,16H_2O$ (A in the Table) is the stable solid phase and has an *X*-ray powder photograph identical with that of $Al_2(SO_4)_3,16H_2O$. The analytical values actually correspond more nearly to a 15-hydrate, but in view of the *X*-ray data, solid A must be the 16-hydrate. Between 10 and 30% of acid, a second form of the 16-hydrate (B in the Table) is obtained, and although the analytical values for A and B differ slightly, close similarity of *X*-ray powder photographs and identity of crystal

habit (small violet elongated hexagonal plates) make it practically certain that the two have the same stoicheiometric composition and very similar geometrical configurations. In the range 30—45% of acid, the solid phase is the 14-hydrate (C in the Table). This was obtained only from solutions which initially were highly supersaturated, and occurs as minute, pale blue needles with a characteristic *X*-ray powder photograph. A tracer experiment with radiocæsium (cf. Taylor and Scott, *Nature*, 1951, **168**, 520) showed that phase C could not contain more that about 3% of sulphuric acid, and was therefore most unlikely to be an acid sulphate. Although no further solid phases could be obtained at higher acid concentrations even after 6 months' stirring, heating an approximately 5% chromic sulphate solution in concentrated

The system $Cr_2(SO_4)_3$–H_2SO_4–H_2O at 245°.

Solution		Dry solid phase			Solution		Dry solid phase		
$Cr_2(SO_4)_3$, %	H_2SO_4, %	$Cr_2(SO_4)_3$, %	H_2SO_4, %	Solid phase	$Cr_2(SO_4)_3$, %	H_2SO_4, %	$Cr_2(SO_4)_3$, %	H_2SO_4, %	Solid phase
39·05	0·0	58·77	0·0	A	13·52	31·08	38·45 *	13·39 *	B
—	—	59·45	0·0	A	8·48	38·26	27·41 *	24·05 *	C
30·80	7·06	58·80	0·83	A	7·31	43·21	60·71	0·78	C
26·51	11·68	59·83	0·0	B	—	—	60·31	0·49	C
23·15	15·90	59·40	0·0	B	—	—	60·62	1·08	C
19·70	20·73	—	—	B	—	—	81·9 †	~18	Anhyd.
17·10	24·27	60·4	0·17	B	—	—	82·6 †	~17	Anhyd.

* Moist solid phase. † Temperature ~300°.

Solid phases: A and B = two forms of $Cr_2(SO_4)_3,16H_2O$ [Calc.: $Cr_2(SO_4)_3$ = 57·6%].
C = $Cr_2(SO_4)_3,14H_2O$ [Calc.: $Cr_2(SO_4)_3$ = 60·9%].

acid to the b. p. readily gave the anhydrous sulphate as a salmon-pink microcrystalline solid, whose *X*-ray powder photograph showed exactly the same pattern of spacings as that of anhydrous aluminium sulphate, the absolute values of the spacings being a few units % greater. The solid probably contains considerably more intercrystallite sulphuric acid than the corresponding aluminium compound. Also, a series of solid solutions of composition $(Al,Cr)_2(SO_4)_3,H_2SO_4,2H_2O$ was obtained by heating mixtures of aluminium and chromic sulphates in 80% sulphuric acid till fuming commenced. Each member of the series gave an *X*-ray powder photograph identical with that of the parent aluminium compound, but the crystal habit was quite different: small pale green needles (colour deepening with chromium content) instead of colourless regular hexagonal plates. With a molecular ratio $Cr_2(SO_4)_3 : Al_2(SO_4)_3 = 9$ in the liquid phase, the precipitated solid solution contained not more than 3 atoms of chromium to every 7 of aluminium, and it therefore appears unlikely that a pure chromium 1,1,2 compound could be prepared. Attempts to prepare acid chromic sulphates by adding " AnalaR " acetone to solutions containing about 10% of $Cr_2(SO_4)_3$ and 75—90% of H_2SO_4, and which had been stirred previously at 25° for several months, gave green, exceedingly deliquescent precipitates. These contained only 2—3% of free acid, and by *X*-ray powder photographs were shown to be amorphous. Apart from the 1,1,2 solid solutions, these were the only green solid phases encountered in this work; on the other hand, all saturated liquid phases were deep green.

UNIVERSITY OF EDINBURGH.

[*Received, April 7th*, 1953.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

Preprinted from the Journal of the Chemical Society,
August 1952, (616), pages 3218—3224.

616. *Phase Equilibria in Sulphonic Acid–Water Systems.*

By Duncan Taylor and George C. Vincent.

Solubility and vapour-pressure relations for the systems $X{\cdot}C_6H_4{\cdot}SO_3H$–$H_2O$, where X = H, *o*-Me, *p*-Me, *p*-NO_2, *p*-F, *p*-Cl, *p*-Br, have been measured, 20 hydrates identified, and several heats of solution and of dissociation calculated. Dingemans's treatment of three-phase data at transition points of anhydrous polymorphs has been extended to inter-hydrate transitions, thus providing heats of dissociation independently of dissociation pressures. The results indicate a greater stability of monohydrates relatively to higher hydrates, in agreement with probable ionic structures for the former.

Williamson (*Trans. Faraday Soc.*, 1944, **40**, 421), in calculating heats of solution from solubility and activity data, took his examples largely from inorganic compounds. The same applies to the work of Dingemans and his co-workers (*Rec. Trav. chim.*, 1943, **62**, 625, 653) on three-phase equilibria in two-component systems and that of Pedersen (*Acta Chem. Scand.*, 1949, **3**, 65) on the calculation of hydrate dissociation pressures from saturated-solution vapour pressures. The following investigation involving benzene-, toluene-*o*- and -*p*-, and *p*-nitro-, *p*-fluoro-, *p*-chloro-, and *p*-bromo-benzene-sulphonic acids was carried out as a specific application, and in certain cases test, of the above theoretical work in aqueous systems of highly soluble organic compounds. It was desired first to establish from solubility measurements which hydrates were formed, and then to determine vapour-pressure data for both saturated and unsaturated solutions to allow (1) calculation of heats of solution by Williamson's procedure, (2) comparison of the observed temperatures of pressure maxima on the three-phase curves with those calculated from an equation of Dingemans *et al.*, and (3) calculation of hydrate dissociation pressures, and hence heats of dissociation, from Pedersen's equations. It was also proposed to extend Dingemans's calculations of heats of transition of polymorphs, using three-phase data, to include the case of inter-hydrate transitions. Heats of dissociation would thus be available without the need for solid–vapour equilibrium data, which are difficult to determine, or metastable equilibrium data as required in Pedersen's calculation. Furthermore, in view of a possible analogy with sulphuric and perchloric acids, for whose monohydrates ionic structures have been proposed (Volmer, *Annalen*, 1924, **440**, 200; Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261), direct determinations of monohydrate dissociation pressures were planned to confirm their expected high stability. Little appears to have been published about $X{\cdot}C_6H_4{\cdot}SO_3H$–$H_2O$ systems apart from the melting points of some doubtful hydrates (Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, 1943).

Experimental

Preparation and Purification of Sulphonic Acids.—Benzenesulphonic acid. The B.D.H. 32% w/v solution was caused to crystallise fractionally at room temperature over phosphoric oxide in a vacuum-desiccator, the main impurity being iron which readily separated as the ferric salt from early fractions. Four-fold crystallisation gave the free acid as colourless deliquescent plates, m. p. 52·5°, whose equivalent by titration with standard barium hydroxide corresponded exactly to the monohydrate. Owing to darkening in bright daylight, the acid was stored in the dark and used only in subdued light.

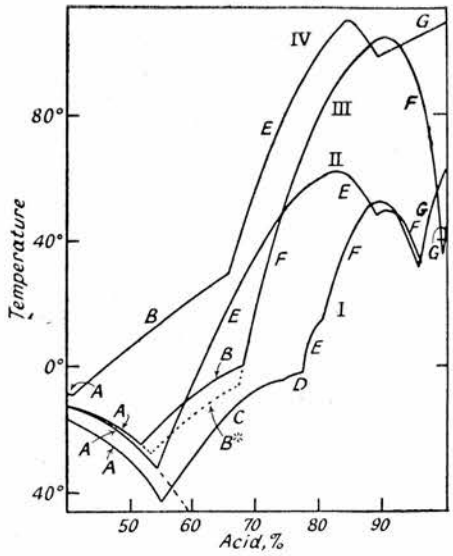
*Toluene-*o- *and* -p-*sulphonic acids.* Tests showed that the B.D.H. products could be used satisfactorily without further purification. The *p*-acid had m. p. 104·8° and its equivalent corresponded exactly to the monohydrate; the *o*-acid had m. p. 62·1°, with equivalent exactly that of the dihydrate. Repeated crystallisation from water did not give better products or significantly alter certain check solubility results.

p-*Nitrobenzenesulphonic acid.* Bell's method (*J.*, 1928, 2776) was used and the acid obtained in the pure state *via* the sulphonyl chloride. The latter was crystallised to a sharp m. p. of 77° and then hydrolysed with distilled water, and the resulting solution was evaporated at room

temperature over solid potassium hydroxide in a vacuum-desiccator till hydrogen chloride was undetectable. The free acid melted sharply at 110·2° and its equivalent was exactly that of the dihydrate.

p-*Fluorobenzenesulphonic acid.* Fluorobenzene, prepared by Balz and Schiemann's method (*Org. Synth.*, 1939, **13**, 46), was sulphonated in the cold with 10% oleum. Treatment with barium carbonate followed by phosphorus pentachloride gave the sulphonyl chloride, which was vacuum distilled; it had m. p. 33·7°, and a mixed m. p. with a sample of pure *p*-fluorobenzenesulphonyl chloride 33·9°. The free acid, obtained by hydrolysis in the same manner as

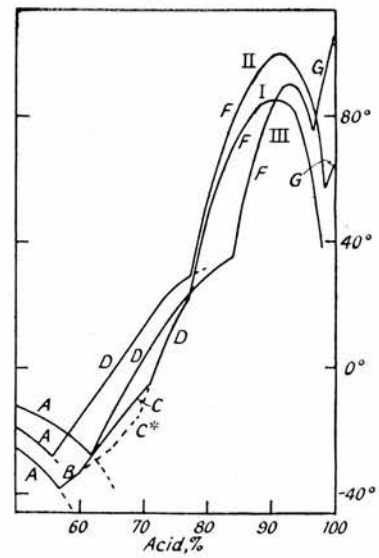
FIG. 1. *Solubility of sulphonic acids.*



I, Benzene-. *II, Toluene-o-.*
III, Toluene-p-. *IV, p-Nitrobenzene-.*

*Solid phases: A = ice, B = tetrahydrate, C = trihydrate, D = 2·5-hydrate, E = dihydrate, F = monohydrate, G = anhydrous acid, * = metastable form.*

FIG. 2. *Solubility of p-halogen-substituted benzenesulphonic acids.*



I, Fluoro-. *II, Chloro-.* *III, Bromo-.*
Solid phases as in Fig. 1.

the *p*-nitro-acid, melted at 85·8°, and its equivalent corresponded exactly to the monohydrate.

p-*Chlorobenzenesulphonic acid.* This acid was prepared from chlorobenzene in a similar manner to the fluoro-acid. The intermediate sulphonyl chloride melted at 53°, and the free acid at 100·3° (Found: equiv., 210·3. Calc. for $C_6H_5O_3SCl,H_2O$: equiv., 210·6).

p-*Bromobenzenesulphonic acid.* The B.D.H. sulphonyl chloride, m. p. 75·5°, was hydrolysed and the free acid obtained as for the *p*-nitro-acid; m. p. 90·2° (Found: equiv., 255·4. Calc. for $C_6H_5O_3SBr,H_2O$: equiv., 255·1).

All the above sulphonic acids dissolved completely in water and contained no inorganic matter, as shown by negligible residues in sulphated ash tests. For some of the solubility measurements, sulphonic acids containing less water than the above hydrates were required. In the cases of the *o*-Me, *p*-F-, *p*-Cl-, and *p*-Br-acids, dehydration was effected rapidly without decomposition by heating *in vacuo* just above the m. p. of the initial hydrate. The *p*-NO_2-acid dihydrate was completely dehydrated in 24 hours at 55° *in vacuo* over phosphoric oxide, benzenesulphonic acid monohydrate required 6 weeks at room temperature, and the *p*-Me acid monohydrate required 6 months at 35°. Higher temperatures for periods of more than a few hours were precluded owing to slight decomposition.

Solubility Determinations.—Since these covered a wide range of temperatures and compositions, the synthetic method was used. Sulphonic acid–water mixtures were prepared by weight in small test-tubes which were then sealed and attached to a simple wire framework. The latter was gently rocked, and thermostatic control was provided by manually operated solid carbon dioxide–ethanol, water, or dibutyl phthalate baths according to the temperature required. Supercooling was very pronounced in all cases, and accordingly, mixtures were first

completely melted, then cooled and frozen out rapidly by touching the tube with solid carbon dioxide to produce small crystals, and the temperature of complete solution approached from below with careful attention to the rate of heating, after which the contents of the tubes were titrated with standard barium hydroxide to give the exact composition. The maximum permissible rates were 0·25° per hour below 10°, 1° per hour between 10° and 50°, and 2° per hour above 50°, calibrated thermometers being used throughout. Mixtures were heated above room temperature for the minimum length of time, in which circumstances no decomposition with the formation of sulphuric acid occurred. Where metastable crystals were encountered, the temperature of the initial freezing out was selected so as to produce the desired solid phase. For economy reasons in a few cases, several solution points were determined with the same sample of acid in a bulb of one-inch diameter, to which known amounts of water could be added with a pipette *via* a ground-glass joint and tap. For those parts of the curves between the m. p.s of congruent hydrates and 100% acid, it was frequently more convenient to start with the hydrate in the test-tube or bulb and remove water by evacuation than to prepare mixtures from anhydrous acid and water. For toluene-*o*-sulphonic acid, mixtures in the range 95·7—100% acid could not be induced to crystallise under any conditions, cooling merely producing a glass, and the same applies to the 98—100% range for the fluoro-acid. From Figs. 1 and 2 only the congruent mono- and di-hydrates can be identified directly. The composition of all other hydrates, both stable and metastable, was determined by direct titration : samples were isolated by filtration through sintered-glass filters previously cooled to the appropriate temperature and drying with filter-paper cooled to the same temperature. The number of molecules of water of crystallisation always corresponded very closely to whole numbers or to 2·5, and no results were obtained which were not in harmony both with the solubility curves and with neighbouring hydrates. Results are given in Table 1. In general, Figs. 1 and 2 confirm the expected high stability of monohydrates relatively to higher hydrates.

TABLE 1. *Solubility of substituted benzenesulphonic acids in water.*

$C_6H_5\cdot SO_3H$		o-$C_6H_4Me\cdot SO_3H$		p-$C_6H_4Me\cdot SO_3H$		p-$NO_2\cdot C_6H_4\cdot SO_3H$	
Temp.	Acid, %	Temp.	Acid, %	Temp.	Acid, %	Temp.	Acid, %
− 1·5°	10·42*a*	− 0·7°	10·26*a*	− 2·0°	9·67*a*	− 3·0°	18·88*a*
− 4·9	21·30*a*	− 3·4	19·56*a*	− 4·0	19·63*a*	− 5·1	30·04*a*
−11·5	33·9*a*	− 7·2	30·42*a*	− 7·5	29·45*a*	− 8·5	39·74*a*
−22·0	45·06*a*	−12·8	40·38*a*	−13·5	41·74*a*	− 8·3	41·22*b*
−29·8	50·23*a*	−25·0	51·37*a*	−23·0	50·72*a*	− 1·0	46·06*b*
−40·4	54·49*a*	−30·5	53·56*a*	−23·5	50·97*a*	10·8	53·94*b*
−40·8	55·91*c*	−33·3	54·81*a* ‡	−24·5	51·40*a* ‡	16·0	56·92*b*
−29·0	59·96*c*	−37·0	56·10*a* ‡	−25·0	51·82*a* ‡	26·3	63·33*b*
−18·5	64·18*c*	−39·4	57·12*a* ‡	−25·5	52·00*a* ‡	36·6	66·31*e*
−10·0	68·87*c*	−44·5	59·16*a* ‡	−25·6	52·14*a* ‡	56·6	69·88*e*
− 5·9	72·14*c*	−25·0	55·69*e*	−18·5	54·87*b*	75·5	73·47*e*
− 4·7	74·44*c*	−13·0	58·51*e*	− 5·9	62·56*b*	90·2	77·27*e*
− 4·0	74·87*d*	0·8	61·17*e*	− 3·4	64·49*b*	110·2	84·92*e*
− 3·3	75·82*d*	16·8	64·95*e*	− 2·2	65·59*b*	106·8	86·50*e*
− 2·5	76·40*d*	31·2	68·58*e*	− 1·0	66·90*b*	100·5 †	90·83*g*
− 2·3	77·61*d*	50·0	74·78*e*	−27·0	53·20*b* *	105·0 †	96·13*g*
2·2	77·61*e*	56·0	77·07*e*	−26·0	54·09*b* *	110·0 †	100·0*g*
7·5	78·54*e*	61·2	80·90*e*	−16·5	59·48*b* *		
13·7	80·04*e*	62·0	83·07*e*	−10·5	63·60*b* *		
15·1	80·52*e*	60·4	85·07*e*	− 8·5	65·0*b* *		
21·3	81·10*f*	54·0	87·64*e*	− 7·0	66·80*b* *		
31·0	82·66*f*	48·2	89·23*e*	− 6·5	66·89*f* ‡		
39·5	84·39*f*	48·5	89·32*f*	− 1·5	67·58*f* ‡		
49·0	87·05*f*	49·0	89·87*f*	1·5	68·06*f*		
52·4	89·60*f*	49·6	91·11*f*	20·1	70·20*f*		
49·0	92·15f	48·6	92·05*f*	38·8	72·50*f*		
39·8	94·04*f*	45·7	93·30*f*	55·2	75·23*f*		
32·6	95·35*f*	38·6	94·66*f*	78·4	79·55*f*		
31·4	95·51*g*	32·5	95·65*f*	89·9	82·38*f*		
42·6	96·74*g*			101·1	86·98*f*		
56·0	98·42*g*			104·8	90·53*f*		
61·3	99·56*g*			102·9	92·39*f*		
				89·1	95·37*f*		
				73·9	97·36*f*		
				45·3	99·02*f*		
				36·5	99·73*g*		
				40·5	99·87*g*		
				42·5	99·97*g*		

TABLE 1 (*continued*).

p-$C_6H_4F{\cdot}SO_3H$		*p*-$C_6H_4Cl{\cdot}SO_3H$		*p*-$C_6H_4Br{\cdot}SO_3H$	
Temp.	Acid, %	Temp.	Acid, %	Temp.	Acid, %
− 4·9°	19·77*a*	− 3·0°	19·08*a*	− 1·9°	14·96*a*
−15·0	39·81*a*	− 6·5	31·96*a*	− 4·5	30·21*a*
−20·5	45·79*a*	−12·5	43·76*a*	− 9·0	45·07*a*
−28·5	51·84*a*	−19·5	50·04*a*	−12·5	50·74*a*
−36·4	55·63*a*	−23·5	53·07*a*	−16·0	54·03*a*
−38·5	56·45*a*	−27·5	55·44*a*	−19·5	56·94*a*
−43·0	58·34*a* ‡	−30·0	56·47*a* ‡	−26·5	61·28*a*
−38·0	57·42*b*	−26·0	56·47*d*	−29·5	62·46*a* ‡
−35·4	58·34*b*	−20·0	58·49*d*	−31·5	63·39*a* ‡
−34·4	59·21*b*	−11·0	61·71*d*	−38·0	65·21*a* ‡
−32·5	60·53*b* ‡	− 2·2	64·71*d*	−21·0	63·41*d*
−30·5	61·38*b* ‡	10·6	69·34*d*	−10·5	65·97*d*
−26·4	64·54*b* ‡	22·9	73·60*d*	0·0	68·95*d*
−24·0	66·25*b* ‡	27·6	75·98*d*	12·5	72·97*d*
−21·4	64·54*c*	30·8	78·75*d* ‡	19·9	75·25*d*
−18·5	65·25*c*	41·0	78·75*f*	27·6	79·16*d*
−13·0	67·56*c*	51·9	79·80*f*	34·6	83·49*d*
− 7·4	69·71*c*	70·1	82·54*f*	43·8	84·78*f*
−22·5	66·25*c* *	80·4	84·55*f*	60·2	86·72*f*
−19·5	67·56*c* *	88·8	86·12*f*	71·2	67·92*f*
−17·9	68·13*c* *	99·9	90·90*f*	80·3	89·78*f*
−15·5	69·15*d*	100·2	91·94*f*	86·2	91·05*f*
− 3·9	71·22*d*	96·7	93·78*f*	90·2	92·99*f*
1·0	72·02*d*	89·0	95·83*f*	87·2	94·75*f*
10·1	74·03*d*	73·3	97·68*f*	78·5	96·18*f*
21·3	76·95*d*	59·8	98·31*f*	76·6	96·43*f*
22·1	77·14*f*	59·0	99·02*g*	82·3	97·21*g*
35·4	78·38*f*	62·4	99·54*g*	89·6	98·00*g*
54·2	81·06*f*			93·1	98·45*g*
71·2	84·33*f*			97·6	98·90*g*
80·0	86·72*f*				
85·5	90·07*f*				
85·2	91·64*f*				
81·0	94·06*f*				
74·5	95·01*f*				
54·3	97·24*f*				
41·4	98·03*f*				

Solid phases: *a* = ice; *b* = tetrahydrate; *c* = trihydrate; *d* = 2·5 hydrate; *e* = dihydrate; *f* = monohydrate; *g* = anhydrous acid.

* Metastable form. † With decomp. ‡ Metastable.

Vapour-pressure Determinations.—The vapour pressures of saturated and unsaturated solutions were measured by a static procedure. The apparatus consisted of a flat-bottomed reaction vessel attached *via* taps and glass sprials to a water reservoir and a wide-bore 15-cm. mercury manometer whose levels were read to ±0·02 mm. with a travelling microscope. The spirals and a glass marble in the reaction vessel allowed gentle agitation of its contents to assist attainment of equilibrium. The system could be evacuated to less than 0·001 mm. of mercury with an oil pump, and was immersed, with the exception of the water reservoir, in a glass-sided water thermostat controlled with electronic relays to better than 0·05°. Below room temperature, a 0° cooling coil was used, and above 80° the water was replaced by dibutyl phthalate. The use of Silicone high-vacuum grease on joints and taps allowed reliable measurements up to 96°. Measurements above this temperature were impracticable owing to slight seepage of dibutyl phthalate into the apparatus, and below 9° because of the very long time to reach equilibrium. Solutions were repeatedly boiled out *in vacuo* to remove dissolved air, compositions being adjusted as desired with de-gassed water from the reservoir. Equilibrium was approached first from below and then from above the equilibrium pressure, and a third time in the case of saturated solutions after a further brief evacuation. The results of these separate experiments, each of which required a maximum of 24 hours, always agreed. Corresponding temperatures and pressures were measured for saturated solutions from beyond the pressure maximum on the mono- or di-hydrate curves, as the case may be, to below the transition to the next highest hydrate.

Measurements at 50° on unsaturated solutions, whose compositions were determined by titration, covered a short composition range up to and including saturation. In no case was more than a minute trace of free sulphuric acid detected in the solutions at the end of an

experiment. Previous tests using distilled water gave vapour pressures agreeing within the limits of the microscope with values given in International Critical Tables, **3**, 210, thus confirming the accuracy of the procedure. In Tables 2 and 3 all pressures are given in mm. of mercury corrected to 0°.

TABLE 2. *Vapour pressure (mm. Hg) of saturated aqueous solutions of substituted benzenesulphonic acids.*

$C_6H_5\cdot SO_3H$		*o*-$C_6H_4Me\cdot SO_3H$		*p*-$NO_2\cdot C_6H_4\cdot SO_3H$		*p*-$C_6H_4F\cdot SO_3H$		*p*-$C_6H_4Cl\cdot SO_3H$		*p*-$C_6H_4Br\cdot SO_3H$	
Temp.	Mm.	Temp.	Mm.	Temp.	Mm.	Temp.	Mm.	Temp.	Mm.	Temp.	Mm.
9·0°	1·24*e*	25·0°	12·55*e*	21·0°	12·93*b*	12·0°	3·21*d*	22·0°	6·62*d*	20·1°	4·74*d*
13·0	1·65*e*	35·0	20·32*e*	23·0	14·25*b*	14·0	3·49*d*	24·0	7·43*d*	26·0	6·63*d*
15·0	1·86*e*	45·0	30·09*e*	25·0	15·60*b*	16·0	3·84*d*	26·0	8·26*d*	28·0	7·39*d*
16·0	1·95*e*	55·0	39·85*e*	27·0	16·87*b*	18·0	4·16*d*	28·0	9·15*d*	30·0	8·20*d*
17·1	2·02*e*	57·0	40·66*e*	28·0	17·55*b*	20·0	4·54*d*	29·0	9·59*d*	32·0	9·02*d*
18·0	2·05*e*	58·0	41·03*e*	29·05	18·44*e*	22·0	4·98*f*	30·0	10·13*f*	35·0	10·51*f*
18·95	2·12*f*	58·5	41·05*e*	31·0	20·41*e*	24·0	5·62*f*	32·0	11·28*f*	38·0	12·10*f*
23·05	2·69*f*	59·0	41·03*e*	33·0	22·66*e*	28·0	6·91*f*	35·0	13·09*f*	40·0	13·24*f*
31·0	3·94*f*	60·0	40·90*e*	40·0	31·75*e*	35·0	9·80*f*	39·8	16·22*f*	50·0	20·27*f*
39·0	5·14*f*			50·0	49·58*e*	55·0	22·65*f*	60·0	38·19*f*	60·0	29·32*f*
43·0	5·69*f*			65·0	91·64*e*	70·0	38·06*f*	80·1	73·30*f*	70·0	39·60*f*
46·0	5·90*f*			79·0	143·4*e*	75·0	42·01*f*	88·9	85·59*f*	80·1	52·25*f*
48·0	5·98*f*					77·1	43·03*f*	91·0	47·48*f*	83·9	53·89*f*
50·0	5·19*f*					79·0	43·72*f*	93·4	88·41*f*	84·4	53·91*f*
						80·0	43·74*f*	94·3	88·24*f*	84·95	53·89*f*
Solid phases : As in Table 1.						83·1	41·37*f*	96·2	87·00*f*	85·8	53·35*f*

TABLE 3. *Vapour pressure (mm. Hg) of unsaturated aqueous solutions of substituted benzenesulphonic acids at 50·0°.**

$C_6H_5\cdot SO_3H$		*o*-$C_6H_4Me\cdot SO_3H$		*p*-$C_6H_4Me\cdot SO_3H$		*p*-$NO_2\cdot C_6H_4\cdot SO_3H$	
Mm.	*m*	Mm.	*m*	Mm.	*m*	Mm.	*m*
14·23	27·23	42·89	14·38	46·44	13·03	61·02	8·312
11·53	30·18	40·89	15·02	44·92	13·60	57·50	8·991
9·11	33·36	39·99	15·27	43·86	14·01	54·93	9·543
8·34	34·18	38·48	15·80	41·44	14·69	53·99	9·831
7·15	38·07	37·87	16·14	39·37	15·45	53·56	9·959
6·37	40·16	36·56	16·85	37·38	16·12	52·55	10·22
6·18	41·78	36·11	17·11	36·87	16·29	50·82	10·58
5·88	42·24	35·86	17·22 †	35·90	16·60	50·43	10·66
5·91	43·65 †			35·33	16·83 †	49·66	10·90 †

p-$C_6H_4F\cdot SO_3H$		*p*-$C_6H_4Cl\cdot SO_3H$		*p*-$C_6H_4Br\cdot SO_3H$	
Mm.	*m*	Mm.	*m*	Mm.	*m*
24·96	20·03	33·23	16·54	24·90	20·61
23·48	20·55	31·56	17·48	22·25	22·21
22·61	20·88	30·09	18·06	21·85	22·58
22·04	21·30	29·23	18·45	21·41	23·09
21·51	21·72	28·21	18·96	20·91	23·64
20·50	22·21	27·55	19·27	20·21	24·73 †
19·42	23·07	26·63	19·74		
18·63	23·45 †	25·57	20·24 †		

* *m* = G.-mole of solute per 1000 g. of water. † Saturated.

Solid phases at saturation : monohydrate for benzene, *p*-CH_3, *p*-F, *p*-Cl, *p*-Br; dihydrate for *o*-CH_3 and *p*-NO_2.

Dissociation Pressure of Monohydrates.—The same apparatus was used as for solution vapour pressures. Monohydrate was crystallised *in vacuo* in the reaction vessel, and approximately half the water of crystallisation removed by prolonged evacuation before allowing the system to come to equilibrium. The times required ran into months and frequently at the end of an experiment traces of free sulphuric acid could be detected. Reliable results were obtained in two cases only.

For benzenesulphonic acid monohydrate, the dissociation pressures were :

Temp.	24·00°	24·90°	25·90°	26·85°	27·90°	29·10°	29·85°
P, mm. Hg	0·096	0·105	0·120	0·140	0·155	0·175	0·200

Each of these pressures was the average of ten readings. They do not deviate by more than about 3% from the equation $\log_{10} P = -4922/T + 15{\cdot}54$, the heat of dissociation being 22·5 kcal./mole. Results (average of 10 readings) for the *p*-bromo-acid were :

Temp.	40·0°	50·0°	54·8°
P, mm. Hg	0·75	1·54	2·11

Agreement is better than 1% with the equation $\log_{10} P = -3087/T + 9{\cdot}743$, giving a heat of dissociation of 14·1 kcal./mole. Attempts to approach equilibrium by adding water vapour to a pressure initially greater than the dissociation pressure were vitiated by rapid adsorption on the anhydrous acid phase. For the *p*-bromo-acid, adsorption equilibrium pressures (average of 10 readings) were :

Temp.	41°	45°	50°	55·1°	60·9°	65·2°	67·0°	69·9°	72·04°
P, mm. Hg	0·26	0·34	0·54	0·86	1·21	1·84	2·11	2·44	2·84

They agree closely with the equation $\log_{10} P = -3663/T + 11{\cdot}07$. The pressure remained at the low adsorption value for several hours before very slowly rising to the true dissociation value.

Pressure Maxima on the Three-phase Curves.—Below are given the observed maxima and those calculated from Dingemans's equation $1/T_{max.} = 1/T_f + 0{\cdot}00021$, where T_f is the m. p. in °K of the stable solid phase. Dingemans has shown (*loc. cit.*) that this equation applies with remarkable success to inorganic compounds where $T_{max.}$ is 20—30° less than T_f. In the present work $T_{max.}$ is close to T_f, and failure is marked :

Acid	T_f,°c	$T_{max.}$, obs.,°c	$T_{max.}$, calc.,°c	Acid	T_f,°c	$T_{max.}$, obs.,°c	$T_{max.}$, calc.,°c
† $C_6H_5\cdot$	52·5	48·0	31·7	† *p*-Cl·$C_6H_4\cdot$	100·4	93·4	73·4
* *o*-$CH_3\cdot C_6H_4\cdot$	62·2	58·5	40·2	† *p*-Br·$C_6H_4\cdot$	90·3	84·4	64·7
† *p*-F·$C_6H_4\cdot$ ...	85·7	80·8	60·3				

Stable solid phases : * dihydrate, † monohydrate.

Heats of Solution at 50°.—These were calculated from Williamson's equation 49 (*loc. cit.*, Appendix). The data in Table 1 were recalculated in terms of molalities, and $(dm/dT)_{sat.}$ evaluated graphically. The term $\left(\frac{\partial \ln \alpha}{\partial m}\right)_T = \frac{1}{P}\left(\frac{\partial P}{\partial m}\right)_T$, where α and P are respectively the activity and vapour pressure of the solvent, was determined graphically at saturation from the data in Table 3. The heat of solution at saturation is then given by

$$\left(x - \frac{55{\cdot}51}{m}\right) \boldsymbol{R} T^2 \left(\frac{dm}{dT}\right)_{sat.} \frac{1}{P}\left(\frac{\partial P}{\partial m}\right)_T$$

where x is the number of molecules of water of crystallisation in the stable solid phase. Results were as follows, in which estimated errors allow only for errors in drawing tangents :

R in $C_6H_4R\cdot SO_3H$	Heat of soln., kcal./mole	R in $C_6H_4R\cdot SO_3H$	Heat of soln., kcal./mole	R in $C_6H_4R\cdot SO_3H$	Heat of soln., kcal./mole
H, $+H_2O$	1·8 ± 0·2	*p*-NO_2, $+2H_2O$ ...	4·3 ± 0·2	*p*-Cl, $+H_2O$	3·8 ± 0·2
o-Me, $+2H_2O$ ...	5·1 ± 0·3	*p*-F, $+H_2O$	4·3 ± 0·2	*p*-Br, $+H_2O$	1·7 ± 0·1
p-Me, $+H_2O$ ...	6·2 ± 0·2				

Heats of Dissociation of Hydrates Other than Monohydrates.—Full details for the approximate calculation of dissociation pressures from a combination of stable and metastable saturated solution vapour pressures are given by Pedersen (*loc. cit.*). For a selection of hydrates, the calculated pressures and heats of dissociation are given in Table 4. In view of the extrapolation

TABLE 4. *Heats of dissociation.*

Acid	Hydrate equilibrium	Calculations after Pedersen : Temp.	Dissocn. press., mm. Hg	Heat of dissocn., kcal./mole	Heat of dissocn., from ΔH values, kcal./mole
$C_6H_5\cdot SO_3H$	$2H_2O \rightleftharpoons H_2O$	14·0°	1·47	10·5	10·5
		9·0	1·05		
p-$NO_2\cdot C_6H_4\cdot SO_3H$ ...	$4H_2O \rightleftharpoons 2H_2O$	27·0	15·78	14·7	14·0
		22·0	10·43		
p-$C_6H_4F\cdot SO_3H$	$2{\cdot}5H_2O \rightleftharpoons H_2O$	20·0	4·43	15·4	11·4
		15·0	3·21		
p-$C_6H_4Cl\cdot SO_3H$	$2{\cdot}5H_2O \rightleftharpoons H_2O$	27·0	8·70	12·4	9·4
		22·0	6·13		
p-$C_6H_4Br\cdot SO_3H$	$2{\cdot}5H_2O \rightleftharpoons H_2O$	30·0	8·07	12·1	9·1
		25·0	5·73		

of the data in Table 2 required to give vapour pressures of metastable solutions, and the small differences between these and the pressures of stable solutions, the heat of dissociation values are probably not accurate to better than ±1 kcal.

Dingemans's approximate treatment (*loc. cit.*) of heats of transition of polymorphs of anhydrous compounds can be extended to hydrates to give heats of dissociation as follows. In the case of 2·5 hydrate $\rightleftharpoons$ monohydrate equilibria, let 1 mole of saturated solution at the transition point contain x moles of anhydrous acid and $(1 - x)$ moles of water. On isothermal evaporation of the solution at a temperature infinitesimally greater than the transition point,

ΔH_1 + $(1/1 - 2x)$ mole of sat. soln. $\longrightarrow$ 1 mole of water vapour + $(x/1 - 2x)$ mole of monohydrate

where ΔH_1 is the change of heat content accompanying the formation of the saturated solution from solid monohydrate and solvent vapour and may be evaluated from the gradient of the three-phase curve (Glasstone, " Thermodynamics for Chemists," Van Nostrand, 1947, p. 241). Similarly, for crystallisation of the 2·5 hydrate at a temperature infinitesimally lower than the transition point,

$\Delta H_{2\cdot5}$ + $(1/1 - 3\cdot5x)$ mole of sat. soln. $\longrightarrow$ 1 mole of water vapour + $(x/1 - 3\cdot5x)$ mole of 2·5 hydrate.

Rearrangement and subtraction of these two equations gives

$2/3\{(1 - 2x/x)\ \Delta H_1 - (1 - 3\cdot5x/x)\ \Delta H_{2\cdot5}\}$ + 2/3 mole of 2·5 hydrate $\longrightarrow$ 1 mole of water vapour + 2/3 mole of monohydrate

in which the first term is the heat of dissociation of the 2·5 hydrate at the transition point. The dissociation of benzenesulphonic acid dihydrate and of the *p*-nitro-acid tetrahydrate may be treated similarly. In certain cases, to determine the ΔH value the plot of $\log_{10} P$ against $1/T$ results in two very similar gradients above and below the transition point. This introduces no major error, however, since both ΔH quantities are multiplied by composition factors, and the respective products are appreciably different. The data in Tables 1 and 2 being used, the values in Table 4 were obtained for which an accuracy of not more than ± 1 kcal. is claimed. The agreement between these and Pedersen's values is as good as can be expected considering the approximate nature of the treatments. In the case of monohydrates of benzene- and *p*-bromobenzene-sulphonic acids, dissociation pressures are much smaller and heats of dissociation greater than for higher hydrates, thus confirming the higher relative stability of their monohydrates evident from Figs. 1 and 2.

Acknowledgments are due respectively to the D.S.I.R. and Imperial Chemical Industries Limited, for the award of a Maintenance Grant (G. C. V.) and of a Fellowship (D. T.), and to the Moray Endowment Fund for a grant for apparatus.

UNIVERSITY OF EDINBURGH. [*Received, March 28th,* 1952.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD., BUNGAY, SUFFOLK.

Nicht im Handel

Sonderabdruck aus Band XXXVIII, Heft 4, 1951, der

MIKROCHEMIE vereinigt mit MIKROCHIMICA ACTA

Schriftleitung: *M. K. Zacherl*, Wien

Springer-Verlag in Wien

Chemistry Department, University of Edinburgh, Scotland.

Polymorphism and Liquid Crystal Formation of Some Azo- and Azoxy-Compounds.

By

Neil Campbell, Andrew Henderson and **Duncan Taylor.**

With 1 figure.

(Received July 12, 1951.)

Although liquid crystal formation has been the subject of much investigation[1], it is only in recent years that polymorphism in organic compounds has received adequate attention[2]. This is undoubtedly due both to the increasing realisation of the widespread occurrence of the phenomenon and to its ready detection by the modern hot stage microscope. The use of this instrument in the characterisation of organic substances is rapidly developing and it is inevitable in consequence that the purely casual detection of polymorphism will increase. If confusion is to be avoided it is essential that the organic chemist should be fully cognisant not only of the frequency of the appearance of polymorphism, but also of the ease with which under a variety of conditions polymorphs of different melting-point, appearance, and stability may be formed. The examples described below were encountered during studies of isomerism of azo-compounds and were examined by means of the elegant apparatus and methods of *L. Kofler*[8].

Our results are conveniently summarised in the accompanying table and in the sequel we give a short account of each substance. We may here note, however, the general observation that where a substance is slow to crystallise from the melt then polymorphism can be expected.

We can find no mention in the literature of the polymorphism of azoxybenzene, but melting-points for the binary system with azobenzene have been given by two authors[3]. It is of interest that in determining the eutectic points with hydrazobenzene no evidence whatsoever could be found for the formation of a compound (cf. *Le Fevre*[4]) thus providing

additional evidence for the incorrectness of *Hodgson*'s suggestion[5] that *cis*-azobenzene may be such a compound.

In the azoxytoluene series the ortho compound is not polymorphous under ordinary conditions; the meta forms a metastable variety only at very low temperatures; and the para provides an example of the uncommon monotropic liquid crystal formation. The transition of an isotropic liquid occurs at a temperature only very slightly less than the true melting-point of the solid. Very few examples of monotropic liquid crystals have been reported[1], and p : p′-azoxytoluene is the simplest compound so far known to exhibit the phenomenon. p-Azoxyanisole has been examined previously[7, 8], and our temperatures agree with those of *Kofler*, but differ considerably from those of *Bernal*. The metastable form II is too unstable to furnish either a melting-point or eutectic points with reference substances.

Our most interesting substance is o : o′-dichloroazoxybenzene. There are two examples of enantiotropy, viz. I ⇄ III, and III ⇄ II, whilst II is monotropic with respect to I. This is best understood from the diagram, in which the vapour pressures are arbitrary, but the temperatures are known accurately. Rapid cooling of the melt frequently gives forms I and II side by side, and when the slide is kept at room temperatures, form III soon appears, rapidly supercedes II and then more slowly takes over form I.

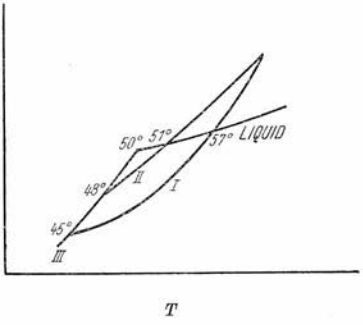


Fig. 1. *V. P.-T* diagram for o : o′-dichloroazoxybenzene.

All three phenylazopyridines are monotropic. The melting points of all the modifications can easily be observed, but some are not sufficiently stable to give eutectic points.

It has been recognised that in polymorphism enantiotropy occurs much less frequently than monotropy[2], and this has been observed in the present work. With o : o′-dichloroazoxybenzene, the reversible transformation of the polymorphs at the transition temperatures can easily be realised, whilst in our examples of monotropy the unstable forms have been observed either to melt before the stable forms, or to change irreversibly to the stable forms at temperatures below the latter's melting-point. These observations, we believe (cf. *Kofler*[8]), constitute the most reliable criteria of the two types of polymorphism, but they can be supplemented by determination of eutectic points given by the polymorphs with suitably chosen reference substances. As may be seen from melting-point diagrams given by *Kofler*[9], a metastable modification in monotropy

will have a lower melting-point and also a lower eutectic point than the stable form, whereas in enantiotropy it is important to realise that either polymorph may have the higher eutectic-point depending on whether the melting-point curve of the reference substance cuts those of the enantiotropic forms above or below the intersection at the transition temperature. In general, eutectic points below the transition temperature are obtained much more easily, but with o : o′-dichloroazoxybenzene one eutectic point above the transition temperature was realised with form I and phenacetine. Unfortunately the corresponding eutectic point with III could not be obtained owing to the rapid transformation III → I.

It is of interest that this behaviour of polymorphs with regard to eutectic points can be deduced from the well-known equations for ideal melting-point curves.

Experimental.

Commercial azoxybenzene was purified by exhaustive chromatography. The azoxytoluenes were prepared by the method of *Zechmeister*[10] and were separated from contaminating azotoluenes by prolonged chromatography. Pure *p*-azoxyanisole was obtained from British Drug Houses, Ltd. The o : o′-dichloroazoxybenzene was prepared from *o*-chloronitrosobenzene, and the phenylazopyridines by condensation of nitrosobenzene with the appropriate 2-amino-pyridines in alkaline solution. All were chromatographically pure before use. Full details of these preparations will be given elsewhere.

The eutectic points of these substances with reference compounds have already been given in the Table.

Azoxybenzene: very pure, pale yellow crystals, m. p. 37.5° (literature 36°). Rapid cooling of the melt on a microscope slide gives form II as strongly refracting spherulites which on quick heating melt at 29.5°. Spontaneous transformation or seeding gives the needle-shaped form I which is less highly refracting. Equilibrium melting results in form I as well formed needles.

o : o′-*Azoxytoluene:* yellow needles, m. p. 59°. Equilibrium melting gives highly refracting laths. No polymorphism could be detected.

m : m′-*Azoxytoluene:* pale yellow needles, m. p. 36° (literature 38–39°). Rapid cooling of the melt with solid carbon dioxide is necessary to produce the metastable form II as highly refracting spherulites. These are very rapidly superceded by the needle-shaped form I.

p : p′-*Azoxytoluene:* yellow needles which melt sharply to an isotropic liquid at 70°. Slow cooling of the melt gives areas of liquid crystals in which laths of solid start to grow. Very careful heating at this stage results in the disappearance of the liquid crystals before the final melting of the laths.

p-*Azoxyanisole:* all observations agree with those of *Kofler*[8].

o : o′-*Dichloroazoxybenzene:* pale yellow plates. Form I appears as highly refracting broad areas, form II as laths developing radially and form III as fine needles. The interconversion of the three forms has been described above.

4-*Methyl*-2-*phenylazopyridine:* is obtained as red rhombs, m. p. 55°. Cooling of the melt on ice gives form II as radially developing laths and form III as spherulites of fine needles. Both are highly refracting, and II rapidly supercedes III. Seeding the melt with I gives the stable form as dendritic growths, while equilibrium melting produces I as laths with two or more oblique end faces.

Table of Results.

Substance	Behaviour, melting points, and transition points	Eutectic point with		
		Benzil	Azo-benzene	Others
Azoxybenzene	Monotropy: I, 37.5° II, 29.5°	I 26° II < 20°	27° 18°	31.5° (1) 19° (1)
o : o′-Azoxytoluene	No polymorphism, m. p. 59°	43°	37°	
m : m′-Azoxytoluene	Monotropy: I, 36° II, ca. 5°	I 26°	18°	
p : p′-Azoxytoluene	Monotropic liquid crystals: true m. p. 70°. Liquid crystals $\overset{69{\cdot}8^0}{\rightleftarrows}$ isotropic liquid	50°		
p-Azoxyanisole	Monotropy and liquid crystals. Liquid crystals $\overset{135^0}{\rightleftarrows}$ isotropic liquid Solid I $\overset{119^0}{\rightleftarrows}$ liquid crystals Solid II is very unstable but its m. p. is close to 119°	78°		97° (2)
o : o′-Dichloro-azoxybenzene	Enantiotropy and monotropy I, 57°; II, 51°; III, 50° I $\overset{45^0}{\rightleftarrows}$ III III $\overset{48^0}{\rightleftarrows}$ II	I 36° II 40°	29° 33°	55° (3)
4-Methyl-2-phenyl-azopyridine	Monotropy I, 55°; II, 39°; III, 32°	I, 41° II, III < 20°	31° < 20°	
5-Bromo-2-phenyl-azopyridine	Monotropy I, 114°; II, 100°; III, 94°	I, 72° II ca. 66°		99° (3) ca. 89° (3)
3 : 5-Dibromo-2-phenylazopyridine	Monotropy I, 112°; II, 95°	I, 72° II, 66°		97° (3) 88° (3)

(1) Eutectic point with hydrazobenzene.
(2) Eutectic point with acetanilide.
(3) Eutectic point with phenacetine.

5-*Bromo*-2-*phenylazopyridine:* deep red rhombs, m. p. 114°. Rapid cooling gives form III as fine structured spherulites, and on reheating forms II and I appear. Form II advances radially as laths with two oblique end faces, while I grows very rapidly as laths with a single oblique end face. The transformation of the metastable forms is too rapid to allow eutectic points to be obtained accurately.

3 : 5-*Dibromo*-2-*phenylazopyridine:* deep red tablets, m. p. 112°. Quick cooling of the melt gives form II as pale orange, fine grained spherulites which transform on heating into broad red areas of the stable form. The metastable form can also be obtained by crystallisation from light petroleum (b. p. 40–60°) at low temperatures.

Acknowledgments.

Thanks are expressed to the Department of Scientific and Industrial Research for a Maintenance Grant (to A. W. H.); to Imperial Chemical Industries, Ltd., for a Fellowship (to D. T.); and to Mr. *Arthur Hodkin*, B. Sc. for assistance in the preparation of some of the substances examined.

Summary.

The polymorphism of several *substituted* azoxybenzenes and azopyridines has been examined, and the eutectic points of these substances with reference compounds determined. Of special interest are o : o′-dichloroazoxybenzene and p : p′-azoxytoluene, the latter of which provides the simplest example of monotropic liquid crystal formation. No evidence was found for *Hodgson*'s suggestion that *cis*-azobenzene is a compound of azoxybenzene and hydrazobenzene.

Zusammenfassung.

Die Polymorphie verschiedener *substituierter* Azoxybenzole und Azopyridine wurde untersucht und die eutektischen Punkte dieser Substanzen mit entsprechenden Verbindungen bestimmt. Als besonders interessant erwiesen sich o,o′-Dichlorazoxybenzol und p,p′-Azoxytoluol, letzteres als einfachstes Beispiel für die Bildung von monotropen flüssigen Kristallen. Die Annahme *Hodgsons*, *cis*-Azobenzol sei eine Verbindung von Azoxybenzol und Hydrazobenzol konnte nicht bestätigt werden.

Résumé.

On a examiné le polymorphisme de diverses azoxybenzènes et azopyridines substituées et déterminé les points eutectiques de ces substances avec des corps de référence. D'intérêt spécial sont l'oo′-dichloroazoxybenzène et le pp′-azoxytoluène, ce dernier fournissant l'exemple le plus simple de formation de cristaux liquides monotropiques. On n'a pas trouvé de preuve au sujet de la suggestion d'*Hodgson* suivant laquelle le *cis*-azobenzène serait un composé d'azoxybenzène et d'hydrazobenzène.

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Printed in Austria

Preprinted from the Journal of the Chemical Society, April 1953, (257), pages 1281—1285.

257. *Geometrical Isomerism of Azo-compounds.*

By NEIL CAMPBELL, ANDREW W. HENDERSON, and DUNCAN TAYLOR.

cis-2 : 2′- and -3 : 3′-Azopyridine have been prepared and their properties studied. Unsuccessful attempts to isolate the *cis*-forms of other azopyridine derivatives are reported. Methods of characterisation included determination of eutectic points with selected second components by means of contact preparations (Kofler, see below), *X*-ray powder photographs, and measurements of dipole moments. Numerous cases of polymorphism are recorded. The thermal behaviour of *cis*-azobenzene is quite different from that of a mixture of azoxybenzene and hydrazobenzene (cf. Hodgson, *J.*, 1948, 1102).

THE evidence from several laboratories is overwhelmingly in favour of the unstable form of azobenzene being *cis*-azobenzene. Hodgson (*J.*, 1948, 1102) does not accept this, however, and states " a double compound of azoxybenzene and hydrazobenzene exhibits far more convincingly many of the reactions of *cis*-azobenzene." Hodgson's objections have been refuted by Le Fèvre (*Chem. and Ind.*, 1948, **26**, 158), Waters (*ibid.*, p. 301), Bright, Carson, and Dyson (*Research*, 1950, **3**, 185), and Tetlow (*ibid.*, p. 187). In particular Le Fèvre and Souter (*J.*, 1949, 1595) reported that hydrazobenzene and azoxybenzene form a simple eutectic below 20° and this is in agreement with Hyrnakowski's statement (*Atti* 10*th Congr. Intern. Chim.*, 1939, **3**, 197) that azoxybenzene and hydrazobenzene form a mechanical mixture. We have confirmed these findings by comparing the melting behaviour on microscope slides of *cis*-azobenzene films in contact along an edge with films of (*a*) azoxybenzene and (*b*) hydrazobenzene, using Kofler's method of contact preparations (Kofler and Kofler, " Mikromethoden zur Kennzeichnung organischen Stoffe und Stoffgemische," Universitätsverlag, Innsbruck, 1949). We found that azoxybenzene and hydrazobenzene do not form a molecular compound, but give a eutectic at 31·5°. *cis*-Azobenzene forms eutectics with hydrazobenzene and azoxybenzene at 58° and 19° respectively. On the other hand *cis*-azobenzene when repeatedly melted and cooled is gradually converted into the stable *trans*-isomer with which it forms a eutectic (40°). The individuality of the unstable isomer was further demonstrated by *X*-ray powder photographs (Unicam 9-cm. camera, Cu-$K\alpha$ radiation), a unique set of spacings being found. Mixtures of azoxybenzene and hydrazobenzene on the other hand, whether melted together or crystallised together from a solvent, gave only those spacings characteristic of the separate components. These results strongly suggest that the unstable azobenzene is the *cis*-isomer.

Le Fèvre (*J.*, 1951, 1814) obtained evidence for the existence of *cis*-2 : 2′-azopyridine. We have isolated the *cis*-compound by irradiating solutions of 2 : 2′-azopyridine with light from a mercury-vapour lamp and separating the products on a column of silica gel. *cis*-2 : 2′-Azopyridine exists as deep-red needles, m. p. 87°, and forms a eutectic with the *trans*-compound at 56°. When the substance is repeatedly heated and cooled, the m. p. falls to 55—57°, and then increases to 83°. The substance then shows no m. p. depression when mixed with a sample of the pure *trans*-isomer.

Absorption spectra also confirm the *cis-trans*-isomerism of 2 : 2′-azopyridine and closely parallel those of *cis*- and *trans*-azobenzene. The azopyridine absorbs at two wavelengths, *trans*- at 314 mμ (log ε 3·97) and 450 mμ (log ε 2·53), and *cis*- at 284 mμ (log ε 3·87) and 446 mμ (log ε 3·03). The comparable figures for azobenzene are : *trans*- 320 mμ (log ε 4·2) and 450 mμ (log ε 2·5), and *cis*- 305 mμ (log ε 3·4—3·5) and 440 mμ (log ε 3·2) (Winkel and Siebert, *Ber.*, 1941, **74**, 675; Le Fèvre and Wilson, *J.*, 1949, 1106; cf. Le Fèvre and Worth, *J.*, 1951, 1814). No great accuracy is claimed for the *cis*-azopyridine curve as the measurements had to be carried out as rapidly as possible owing to the mobility of the *cis-trans*-equilibrium under the influence of ultra-violet light. About the main features of the curve, however, there is no doubt.

3 : 3′-Azopyridine was likewise obtained both in the *cis*- and the *trans*-form, but here the melting points of the two forms—82° (*cis*) and 140° (*trans*)—differ considerably. The *cis*- is converted into the *trans*-form much more rapidly than with the 2 : 2′-compound. *X*-Ray powder photographs again showed that each *cis*-isomer possessed characteristic spacings.

Unsuccessful attempts were made to isolate the *cis*-forms of 4 : 4′-azopyridine, 3-phenylazopyridine, 2- and 3-*o*-chlorophenylazopyridine, 4 : 4′-dimethyl-2 : 2′-azopyridine, and 5-bromo-2-phenylazopyridine.

Further evidence for the occurrence of *cis*-isomers was obtained from dipole moments, determined with an apparatus described by Henderson and Taylor (*Trans. Faraday Soc.*, 1953, **49**, 92). The values (see Table) for the 2 : 2′- and 3 : 3′-compounds are parallel to those for azobenzene (zero for *trans*, 3 D for *cis*; Le Fèvre and Hartley, *J.*, 1939, 531) and azoxybenzene (1·7 D for *trans*, 4·7 D for *cis*; Gehrckens and Müller, *Annalen*, 1933, **500**, 296). For the other compounds, since the pure *cis*-isomers could not be isolated, only the

Pyridine derivative	Dipole moment (D) *trans*	*cis*	Change in μ after ultra-violet illumination
2 : 2′-Azo	1·77	4·0	—
3 : 3′-Azo	2·40	2·85	—
2-Phenylazo	2·2	—	+0·6
3-Phenylazo	2·3	—	+0·2
4-Phenylazo	2·7	—	−0·1
4 : 4′-Azo	2·0	—	−0·3
4-Methyl-2-phenylazo	2·7	—	+0·4
5-Bromo-2-phenylazo	2·6	—	+0·2
3 : 5-Dibromo-2-phenylazo	1·8	—	+0·2
2-*o*-Chlorophenylazo	2·1	—	+0·8
3-*o*-Chlorophenylazo	2·4	—	+0·3

approximate change in dipole moment after illumination in benzene solution could be evaluated. Le Fèvre and Vine's procedure (*J.*, 1937, 1805) was used, a constant value 0·26 being assumed for β, this being the mean value for eleven solutions of the *cis*- and *trans*-2 : 2′- and -3 : 3′-compounds. [In their equations for the dipole moment, β is defined by $d = d_1(1 + \beta w_2)$ where d and d_1 are the densities of solution and solvent respectively, and w_2 is the weight fraction of the solute.] The individual values of β varied from 0·20 to 0·31, but since all the compounds in the Table are of similar type and since errors in β have only minor importance in the calculation of the dipole moment, the direction of change of the latter after illumination is considered significant. The changes are consistent with *cis*-isomer formation, except possibly for 4-phenylazopyridine and 4 : 4′-azopyridine. However, simple calculations using structures based on the analogous azobenzenes (Robertson and Hampson, *J.*, 1941, 409) show that in these cases a fall in dipole moment on *cis*-isomer formation may in fact be expected owing to the opposing effects of the azo- and ring nitrogen atoms.

A number of our compounds were found to be polymorphous, monotropy greatly predominating over enantiotropy (cf. Campbell, Henderson, and Taylor, *Mikrochem. Mikrochim. Acta*, 1951, **38**, 376). Depending on the stability of the polymorphs, such compounds when examined by the Kofler technique may show several melting points (and eutectic points when in contact with a second component) and this greatly assisted characterisation of the compounds. As second components in the contact preparations, azobenzene, benzil, *p*-nitrophenol, phenylacetic acid and phenacetin were particularly useful. Contact preparations with pairs of azo-compounds revealed many instances of solid solutions, but none involving *cis*-components. With *trans*-components, great similarity of molecular size and configuration was necessary, the methyl groups in the case of 4-methyl-2-phenylazopyridine + 4 : 4′-dimethyl-2 : 2′-azopyridine being enough to disturb the continuous series of solid solutions obtained with the unmethylated compounds.

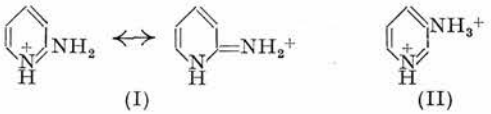
A general method for the preparation of aromatic azo-compounds is the condensation of nitrosobenzenes with primary aromatic amines in glacial acetic acid. Attempts to condense nitrosobenzene with 2-aminopyridine in this way failed, but syntheses were successful with an alkaline condensing agent. This suggests that these reactions are of the aldol type (cf. Schönberg and Michaelis, *J.*, 1937, 627; Bergmann, *ibid.*, p. 1628).

The failure of 2(and 4)-aminopyridine to condense with nitrosobenzene in an acid medium can be attributed to the addition of a proton to the ring-nitrogen atom (see, *e.g.*, Steck and Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397; Mann and Watson, *J. Org. Chem.*, 1948, **13**, 502). This results in a positive charge on the 2-amino-nitrogen atom, as in (I), so that interaction with the cation $C_6H_5\cdot\overset{+}{N}\cdot OH$ is impossible. Such a reason cannot be

$$C_5H_4N\cdot NH_2 + B \rightleftarrows C_5H_4N\cdot NH^- + BH^+$$

$$Ph\cdot\overset{+}{N}\!-\!\bar{O} + C_5H_4N\cdot\bar{N}H \rightleftarrows Ph\cdot\overset{O^-}{N}\cdot NH\cdot C_5H_4N \overset{BH^+}{\rightleftarrows} B + Ph\cdot\overset{OH}{N}\!-\!NH\cdot C_5H_4N \xrightarrow{-H_2O} Ph\cdot N{=}N\cdot C_5H_4N$$

(B is a base).



(I) (II)

advanced to explain the inertness of 3-aminopyridine in acid solution. It is known, however, that in contrast to its isomers 3-aminopyridine forms dihydrochlorides, etc. Consequently in acid media the amino-nitrogen atom is positively charged, as in (II), and thus does not condense with nitrosobenzene.

Experimental

All the thermal data (m. p.s, eutectic points, etc.) were obtained by means of the Kofler hot-stage microscope (Kofler and Kofler, *op. cit.*).

Preparations of Azopyridines.—(a) Oxidation of aminopyridines by sodium hypochlorite (Kirpal and Reiter, *Ber.*, 1927, **60**, 664) can be used when there is no danger of nuclear chlorination. We confirmed that oxidation of 2-aminopyridine by this method gives 2 : 2′-azopyridine and a little 5-chloro-2 : 2′-azopyridine (Kirpal, *Ber.*, 1934, **67**, 70) by purifying the oxidation product by partition chromatography on silica gel. The chloro-compound, m. p. 136°, was quickly washed out, leaving the pure 2 : 2′-azopyridine at the top. This was eluted with ether–ethanol and crystallised from light petroleum (b. p. 60—80°) in deep red needles, m. p. 85—86°. The method was used to prepare the following substances from the appropriate substituted aminopyridines. 5 : 5′-Dibromo-2 : 2′-azopyridine, orange needles (from benzene–light petroleum), m. p. 260° (Found : C, 35·0; H, 1·5; N, 16·3; Br, 47·3. Calc. for $C_{10}H_6N_4Br_2$: C, 35·1; H, 1·8; N, 16·4; Br, 46·7%). Bystrikskaya and Kirsanov (*Chem. Abs.*, 1941, **35**, 4023) give m. p. 235° (decomp.). 3 : 3′ : 5 : 5′-*Tetrabromo*-2 : 2′-*azopyridine* (23% yield) was purified by passing a benzene solution down a column of alumina and separated from benzene in orange needles, polymorphous, m. p. of stable form 103° (Found : C, 24·3; H, 1·7; N, 11·0; Br, 63·0. $C_{10}H_4N_4Br_4$ requires C, 24·0; H, 0·8; N, 11·2; Br, 64·0%). 3 : 3′-Dinitro-2 : 2′-azopyridine (23% yield), red rhombs (from benzene), m. p. 230° (Found : C, 43·9; H, 2·3; N, 30·5. $C_{10}H_6O_4N_6$ requires C, 43·8; H, 2·2; N, 30·7%). 5 : 5′-*Dinitro*-2 : 2′-*azopyridine* (41% yield), brownish-red needles (from benzene), m. p. 220° (Found : C, 44·0; H, 2·7; N, 30·9%). 3 : 3′-Azopyridine, orange needles (from light petroleum), m. p. 140°. 4 : 4′-Azopyridine (41% yield), orange needles, m. p. 108—109°, after purification on alumina and crystallisation from light petroleum (Found : C, 64·6; H, 4·7; N, 30·2. Calc. for $C_{10}H_8N_4$: C, 65·2; H, 4·4; N, 30·4%). den Hertog and Combe (*Rec. Trav. chim.*, 1951, **70**, 588) give m. p. 104—105°.

(b) *Reduction of nitropyridines by alkaline arsenious oxide.* This method gave 2 : 2′-azopyridine, m. p. 85—86° (20% yield); 4 : 4′-*dimethyl*-2 : 2′-*azopyridine* (65% yield), orange needles (from light petroleum), m. p. 149—151°, after purification on alumina (Found : C, 68·0; H, 5·7; N, 26·0. $C_{12}H_{12}N_4$ requires C, 67·9; H, 5·7; N, 26·4%); and 3 : 3′-azopyridine (62%), m. p. 138—140°.

(c) *Condensation of nitrosobenzenes and aminopyridines.* 2-Aminopyridine (5 g.) was added to a warm 50% sodium hydroxide solution (50 ml.) which was then gently heated, and benzene (3 ml.) was added. Nitrosobenzene (6 g.) was added during 10 minutes, with shaking, and the mixture warmed for a further 10 minutes. Extraction with benzene (3 × 100 ml.) gave a solution which was heated with charcoal, filtered, and concentrated under reduced pressure to 100 ml. The concentrate was passed down a column of alumina, development of which with benzene gave a lower zone of nitrosobenzene and azoxybenzene, and an orange-red zone which

was extracted with benzene. Evaporation afforded 2-*phenylazopyridine* (8 g.), red needles (from light petroleum, b. p. 40—60°), m. p. 32—34° (Found: C, 72·1; H, 4·7; N, 22·4. $C_{11}H_9N_3$ requires C, 72·1; H, 4·9; N, 22·9%). Similarly nitrosobenzene and the appropriate aminopyridine gave the following: 5-*bromo*-2-*phenylazopyridine* (86% yield based on the amine), scarlet diamonds, polymorphous, m. p. of stable form 115° (Found: N, 15·8; Br, 30·3. $C_{11}H_8N_3Br$ requires N, 16·0; Br, 30·5%), 3 : 5-*dibromo*-2-*phenylazopyridine* (84%), crimson plates, polymorphous, m. p. of stable form 112° (Found: N, 12·4; Br, 46·8. $C_{11}H_7N_3Br_2$ requires N, 12·3; Br, 46·9%), 4-*methyl*-2-*phenylazopyridine* (68%), red prisms, polymorphous, m. p. of stable form 55° (Found: C, 73·1; H, 5·5; N, 21·1. $C_{12}H_{11}N_3$ requires C, 73·1; H, 5·6; N, 21·3%), 3-*phenylazopyridine* (60%), orange leaflets, polymorphous, m. p. of stable form 52—53° (Found: C, 73·3; H, 4·7; N, 22·4%), and 4-phenylazopyridine (69%), orange leaflets, m. p. 98° (Found: C, 71·6; H, 5·0; N, 23·1%). *o*-Chloronitrosobenzene likewise gives 2-o-*chlorophenylazopyridine* (48%), red needles, m. p. 54—55° (Found: N, 18·8; Cl, 15·8. $C_{11}H_8N_3Cl$ requires N, 19·3; Cl, 16·3%), and 3-o-*chlorophenylazopyridine* (47%), red needles, polymorphous, m. p. of stable form 60° (Found: N, 19·7; Cl, 16·8%). The method fails with aminonitropyridines and 2 : 6-diaminopyridine.

Conversion of trans- *into* cis-*Isomers*.—The *trans*-compounds were dissolved in sodium-dried solvents and irradiated by a Hanovia mercury-vapour lamp. Clamping the reaction flask 18 in. from, and 8 in. above, the lamp gave a slight heating effect which mixed the liquid. In a typical experiment azobenzene (5 g.) was irradiated for 12 hours in benzene (250 ml.). The solution was then chromatographed on alumina (diam. 3 in., depth 1½ in.). The chromatogram was developed with benzene until the strongly adsorbed *cis*-layer was separated from the *trans*-compound. Extraction with benzene containing acetone (20 : 1) and evaporation of the extract at low pressure and temperature gave *cis*-azobenzene, rhombic plates (from light petroleum, b. p. 40—60°), m. p. 71° (*lit.*, 71·4°). A sample when melted and cooled afforded broad, flat needles of *cis*-azobenzene followed by smaller needles of the eutectic mixture, m. p. 40°, penetrating in all directions. Alternate heating and cooling caused the temperature of "final melting" (disappearance of last crystals in the melt) to decrease and then rise again, while the melting began consistently at 40°. In this way the final m. p. decreased from 71° to 51° then rose to 66°. The final solidified melt under the microscope showed the absence of eutectic crystals, and the material gave no m. p. depression with a sample of *trans*-azobenzene, m. p. 68°.

cis-m-Nitroazobenzene, m. p. 69—71° (*lit.*, 70°) was repeatedly melted and cooled. The final m. p. sank to 60°, then rose to 94—95°, which was not altered when the substance was admixed with the *trans*-isomer, m. p. 96°. The latter is polymorphic.

cis-p-Iodoazobenzene separated from light petroleum (b. p. 40—60°) in red leaflets, m. p. 74—76°. Repeated melting and cooling caused the m. p. to fall to 62·5° (eutectic point) and then to rise to 99°, which was unaltered when the substance was mixed with pure *trans*-isomer, m. p. 104°. It is suggested that the substance cited in the literature as the *cis*-compound, m. p. 62° (Cook and Jones, *J.*, 1939, 1309) is in fact the eutectic mixture of *cis*- and *trans*-isomers.

Solid *cis-p*-iodoazobenzene is stable and showed no lowering of m. p. after 3 months in the dark.

cis-2 : 2′-*Azopyridine*.—*trans*-2 : 2′-Azopyridine (2 g.) was irradiated in dry benzene–light petroleum (50 ml.) for 12 hours, then shaken with water, and the non-aqueous solution passed down a column of silica gel (30—40 g. of SiO_2 + 53% of its weight of water in a column 2—5 cm. wide) made up with the same solvent mixture. Development with benzene–light petroleum washed down the *cis*-band, leaving the *trans* as a dull orange layer. The *cis*-solution was evaporated at low temperature and yielded cis-2 : 2′-*azopyridine* (0·25 g.), deep red needles (from light petroleum, b. p. 40—60°), m. p. 87° (Found: C, 65·6; H, 4·3; N, 30·1. $C_{10}H_8N_4$ requires C, 65·2; H, 4·4; N, 30·4%). It forms a mixture with the *trans*-compound, eutectic temperature 56°. Repeated heating and cooling gave the following results:

Disappearance of last crystal (° c)	87	77	80	78	68	67	55	57	75	77	82	84	83	84	83	83	83
Initial melting		75	56	55	50	50	50	38	35	35	35	35	60	55	55	55	

At the final stage the eutectic mixture had practically all disappeared, and the substance showed no m. p. depression when mixed with a sample of pure *trans*-compound. The eutectic value of 35° in some observations can be explained by the assumption that there is a tendency towards polymorphism in either or both the *cis*- and the *trans*-compound.

cis-2 : 2′-Azopyridine is almost insoluble in water whereas the *trans*-compound is extremely soluble (cf. Kirpal, *Ber.*, 1934, **67**, 70). It is suggested that the insolubility of the *cis* is due to

effective screening of the nitrogen atoms in this configuration. The *trans*-compound gives a deep blue colour with ferrous salts, but the *cis*-compound does not. The *trans*-compound in ethanol gives green and white precipitates with copper sulphate and silver nitrate respectively.

cis-3 : 3′-*Azopyridine*.—*trans*-3 : 3′-Azopyridine (1 g.) was irradiated as above and the solution passed down a silica gel column (30 × 2 cm.). Development with water-saturated benzene–light petroleum resulted in rapid passage of the *trans*-compound, m. p. 139° (*lit.*, 142°) down the column. The residual orange zone was eluted with benzene–methanol (100 : 1), evaporation of which at low temperature and pressure gave cis-3 : 3′-*azopyridine*, scarlet rhombs (from light petroleum), m. p. 82° (Found : C, 65·1; H, 4·5; N, 29·9%). Heating the compound above 100° causes small groups of laths to appear. These grow as the temperature is raised until no liquid is left and then melt at 142°, undepressed when the substance is admixed with the *trans*-compound. Clearly the *cis*- is more quickly converted into the *trans*-compound than is the corresponding 2 : 2′-compound.

4-*Methyl*-2-*nitropyridine*.—2-Amino-4-methylpyridine was oxidised by hydrogen peroxide and sulphuric acid (Kirpal and Bohm, *Ber.*, 1932, **65**, 680) to 4-methyl-2-nitropyridine (36% yield), leaflets (from light petroleum, b. p. 60—80°), m. p. 65·5—66·5° (Found : C, 55·2; H, 4·1; N, 20·4. Calc. for $C_6H_6O_2N_2$: C, 52·2; H, 4·4; N, 20·3%). Wiley and Hartman (*J. Amer. Chem. Soc.*, 1951, **73**, 494) give m. p. 61—62°.

Thanks are expressed to the D.S.I.R. for a maintenance grant (to A. W. H.), to Imperial Chemical Industries Limited for a Fellowship (to D. T.), and to the Anglo-Iranian Oil Co. Ltd. and Moray Endowment Fund for grants for chemicals and apparatus.

University of Edinburgh. [*Received, January* 12*th*, 1953.]

Printed in Great Britain by Richard Clay and Company, Ltd.,
Bungay, Suffolk.

Reprinted from the *Transactions of the Faraday Society*,
No. 361, Vol. 49, Part 1, January, 1953

DIELECTRIC CONSTANT METER FOR DILUTE SOLUTIONS

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Received 12*th June*, 1952; *in final form*, 18*th August*, 1952

The circuit diagram of a dielectric constant meter intended for the measurement of dipole moments is described. It is based on the heterodyne beat principle, and the use of a precision condenser to match the capacity of the liquid cell is avoided by calibrating the meter with benzene solutions of nitrobenzene of known dielectric constant. An accuracy of $\pm$ 0·0002 unit was attained over small dielectric constant ranges.

In dipole moment determinations the usual accurate method for measuring the dielectric constant of solutions involves matching the capacity of a suitably designed liquid cell with a precision condenser.[1] The following instrument, constructed during *cis-trans* isomerism studies in the azopyridine series, was specifically designed (i) to avoid the use of such a condenser, and therefore (ii) to eliminate the uncertain capacity changes introduced during its interchange with the liquid cell. The heterodyne beat principle was employed, the beat frequency from a quartz crystal oscillator and a variable oscillator incorporating the liquid cell being matched on a cathode ray oscilloscope with the frequency from a very stable audio-frequency oscillator, the latter being variable over the audio-frequency range by means of an air condenser. The instrument was calibrated by determining the setting of the latter condenser for a series of benzene solutions of nitrobenzene, and the accuracy of the measurements of dielectric constant therefore depended (i) on the reliability of the literature values for nitrobenzene, and (ii) on the reproducibility of the calibration graph. While the useful range of any one calibration was limited by the circuit components, experience showed that both (i) and (ii) were adequate to allow the detection of dielectric constant differences of not less than 0·0002 in benzene solutions of azopyridines of weight fraction 0·002-0·01. Details of the azopyridine work will be published elsewhere.

EXPERIMENTAL

Details of the electrical circuit are given in the figure and table 1. The radio-frequency oscillator incorporating the liquid cell contains a 6A8 heptode arranged to oscillate as a transitron,[2] a type which is capable of high stability. The inductance L_1 is a variable dust-iron cored coil, while the capacitance apart from a very small trimming condenser C_1 is contributed by the liquid cell and coaxial leads. Further stability was ensured by running the valve at a low power (h.t., 100 V), and the oscillator was completely screened from the rest of the assembly. The output is fed to the grid of the " mixer "

valve, a 6K8 triode-hexode, in the triode part of which is arranged a Pierce type oscillator controlled by a quartz crystal at 500 kc/sec. The audio beat frequency from the mixer goes via an R—C amplifier to the *X*-plates of the cathode ray tube. The audio-frequency oscillator of range approximately 0-20 kc/sec is similar to the very stable type described by Clifford,[3] the output after amplification in the second half of the 6SN7 valve being applied to the *Y*-plates of the cathode ray tube. With the exception of the latter, the instrument was operated entirely from batteries and accumulators to avoid instability due to mains voltage fluctuations, and was installed in a thermostated room at $21 \pm 0{\cdot}3°$ C Good quality radio components were used throughout, the wiring being as rigid as possible.

The liquid cell, volume 10 ml, was of the type described by Le Fèvre,[4] with the addition of a coaxial socket rigidly mounted on a polythene plug which was bolted to the flanged top of the cell. It was suitably clamped in a water thermostat at $25 \pm 0{\cdot}1°$ C and could be filled and emptied via side-tubes without any disturbance of the clamp or electrical connections.

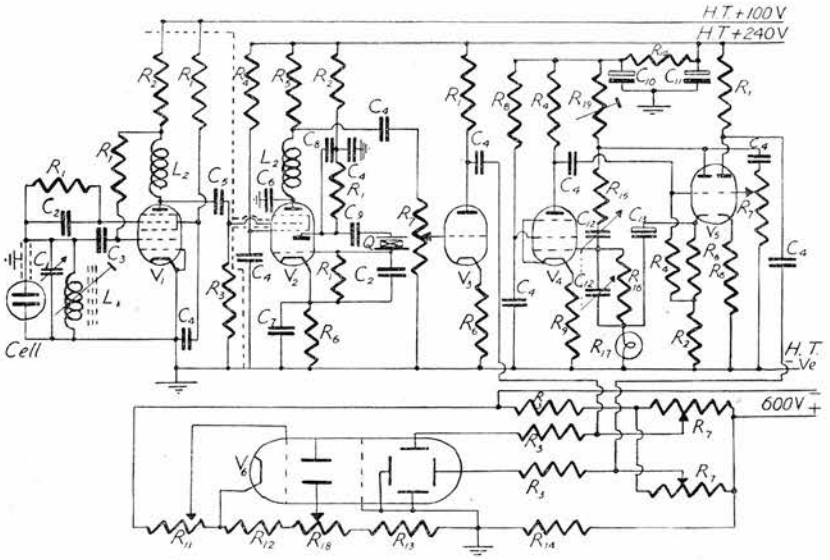

FIG. 1.

With pure dry benzene in the cell, and with condenser C_{12} set to 50·00 divisions on the scale and C_1 set approximately in the middle of its range, the inductance L_1 was adjusted to give a vertical figure-eight Lissajou figure on the cathode ray tube, care being taken to see that the cell oscillator frequency was less than that of the crystal oscillator. The point 50·00 on C_{12} corresponded to an audio-frequency of approximately 750 c/sec, and the beat frequency for the above "zero" setting at dielectric constant $\epsilon = 2{\cdot}2725$ was thus exactly twice this value. An occasional very slight drift of the zero occurred during use, and the instrument was accordingly re-set to scale reading 50·00 with benzene in the cell by means of C_1 immediately before use with a solution. The following sequence for taking readings was always observed:

time	*operation*
0 min	l.t. to valves
4 min 45 sec	l.t. to c.r.t.
5 min	h.t. to valves
5 min 15 sec	h.t. to c.r.t.
5 min 30 sec	adjust C_{12} (or C_1 when setting the zero) to give a figure-eight.

After one reading, the instrument was completely switched off and left for 15 min before taking a second to allow the components to return to room temperature and humidity.

Calibration of the scale on C_{12} against dielectric constant was carried out using very dilute solutions of nitrobenzene, ϵ values for the latter being obtained by straight line

extrapolation of the data of Jenkins [5] and Le Fèvre [6] to $\epsilon = 2{\cdot}2725$ at zero molar fraction. There appears to be no reason to doubt the validity of this extrapolation.[7] The calibration graph was a shallow curve, 30 divisions on C_{12} corresponding to a dielectric constant change from 2·2725 to 2·3340. While C_{12} could be read with the aid of a vernier to $\pm$ 0·02 divisions, re-calibration over a period of weeks gave values reproducible to within $\pm$ 0·0002 in ϵ equivalent to $\pm$ 0·1 divisions on C_{12}. By suitably setting L_1, R_{15} and R_{16}, the calibration graph can be given a similar gradient over other ϵ ranges thus allowing other solvents to be used.

TABLE 1

	resistances		*condensers*
R_1	50 kΩ $\frac{1}{2}$W	C_1	5-10 $\mu\mu$F, variable
R_2	5 kΩ $\frac{1}{2}$W	C_2	100 $\mu\mu$F
R_3	1 MΩ $\frac{1}{2}$W	C_3	0·001 μF
R_4	120 kΩ $\frac{1}{2}$W	C_4	0·1 μF
R_5	200 kΩ $\frac{1}{2}$W	C_5	7 $\mu\mu$F
R_6	1 kΩ $\frac{1}{2}$W	C_6	200 $\mu\mu$F
R_7	500 kΩ, variable	C_7	0·01 μF
R_8	250 kΩ $\frac{1}{2}$W	C_8	20 $\mu\mu$F
R_9	500 Ω $\frac{1}{2}$W	C_9	0·002 μF
R_{10}	4 kΩ $\frac{1}{2}$W	C_{10}	24 $\mu\mu$F 350 V
R_{11}	25 kΩ, variable	C_{11}	8 $\mu\mu$F 350 V
R_{12}	20 kΩ $\frac{1}{2}$W	C_{12}	0·001 μF, variable
R_{13}	150 kΩ $\frac{1}{2}$W	C_{13}	50 $\mu\mu$F 50 V
R_{14}	22 kΩ $\frac{1}{2}$W		
R_{15}	500 kΩ $\frac{1}{2}$W		*valves*
R_{16}	330 kΩ $\frac{1}{2}$W	V_1	6A8 [U.S.A.]
R_{17}	5 watt 230 V Atlas lamp	V_2	6K8 [R.C.A.]
R_{18}	50 kΩ, variable	V_3	6J5 [R.C.A.]
R_{19}	5 kΩ, variable [preset]	V_4	6SJ7 [R.C.A.]
20 % tolerance on fixed resistors		V_5	6SN7 [U.S.A.]
		V_6	C.R.T. E-4103-B-4 [G.E.C.]

Other components

L_1 dust-iron cored variable inductance, 0·2 mH
L_2 radio-frequency choke
Q G.E.C. quartz crystal, 500 kc/sec.

DISCUSSION

In general, the use of a calibration procedure as above would be inadmissible in work of the highest accuracy and especially if absolute ϵ values were required, for not only may the literature values of the calibrating solutions be slightly incorrect, but also no corrections were applied for the several minor sources of error discussed by Few, Smith and Witten.[1] However, for average use in dipole moment calculations, the important quantity is the dielectric constant difference between solvent and solution, and provided the calibration and the other minor sources of error do not change during a series of measurements, this difference is given with an accuracy determined by the slope of the calibration curve.

In order to secure the desired slope the dielectric constant range had to be limited to about 0·06 units, and this in turn limited the range of solution concentrations. For azopyridines with μ values between 2 and 4D, weight fractions between 0·002 and 0·01 could be used, which ruled out any reliable extrapolation of data to infinite dilution. Extrapolation for such dilute solutions is probably unnecessary, and no major error was introduced since μ values calculated by otherwise standard procedure [8, 9] from different sets of data within the above weight fraction range did not differ significantly among themselves. Furthermore, the value obtained for *trans*-2·2′-azo*bis*-pyridine was 1·77 $\pm$ 0·04D while Le Fèvre [10] has reported 1·8D.

Grateful acknowledgements are made to Prof. H. D. Springall, Dr. Neil Campbell and Mr. F. P. Henderson, for advice and discussions, to the Anglo-Iranian Oil Co., Ltd. and the Moray Endowment Fund for grants for apparatus, to the D.S.I.R. for the award of a maintenance grant (to A. W. H.) and to I.C.I. Ltd., for the award of a fellowship (to D. T.).

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PRINTED IN GREAT BRITAIN AT
THE UNIVERSITY PRESS
ABERDEEN

Preprinted from the Journal of the Chemical Society, February, 1955, (5789), pages 489—497.

Kinetics of a Polymorphic Transformation of Azoxybenzene.

By Arthur Hodkin and Duncan Taylor.

[Reprint Order No. 5789.]

A new monotropic polymorph of azoxybenzene has been characterised, and the kinetics of its transformation into the stable form under thin-film conditions have been investigated over the range 0—30°, a photometric method being used for the measurement of transformation rates. With highly purified material, the transformation is strictly linear with time, independent of film thickness, and relatively free from difficulties caused by spontaneous nucleation. The results agree well with the mechanism proposed by Hartshorne for polymorphic transformations, the energy of activation being 22·5 ± 1 kcal./mole (the heat of transition being assumed as 1 kcal./mole), and the temperature-independent factor very large. The activation energy agrees closely with 23 ± 1 kcal./mole, the heat of sublimation of the metastable form. The latter has been determined by an effusion method, the heat of transition being assumed to be as above. An approximate doubling of the rate after exposure to ultra-violet light is reported and discussed. The transformation is shown to parallel that of monoclinic ⟶ rhombic sulphur in several respects.

Little is known of the mechanism of polymorphic transformations and few kinetic measurements of this type have been reported. The scarcity of data is due mainly to the difficulty of finding examples which undergo transformation in an easily measurable fashion. Experience with a polymorph of azoxybenzene (Campbell, Henderson, and Taylor, *Mikrochem. Mikrochim. Acta*, 1951, **38**, 376) suggested that this might be a suitable case for study, and further work has revealed a second monotropic polymorph which is transformed into the stable modification in a manner eminently suitable for kinetic measurements. The results here presented lead to the same mechanism as that proposed by Hartshorne and his co-workers (*Discuss. Faraday Soc.*, 1949, **5**, 149; *J.*, 1951, 1097) for the monoclinic ⟶ rhombic sulphur transformation, *viz.*, one based on the difference in rates of escape of molecules from the two adjacent lattices, and requiring the full latent heat of sublimation of the metastable form as energy of activation.

Experimental and Results.

Preparation and Purification.—Azoxybenzene was prepared by sodium methoxide reduction of pure nitrobenzene and purified by crystallisation from aqueous methanol, followed by chromatography on a benzene–alumina column and a further crystallisation. These operations were carried out under red light owing to the ease with which the pale yellow azoxybenzene developed an orange colour when exposed to white light in contact with solvents (cf. Badger and Buttery, *J.*, 1954, 2243). Final purification was by distillation at a pressure $<10^{-5}$ mm. in a vertical tube (10″ × 1½″), also under dark-room conditions. The impure material in the bottom of the tube was kept molten by means of a water-thermostat at 50°, the lowest temperature at which a reasonable rate of distillation occurred, while the upper half of the tube was cooled to 10°. The condensate obtained during the first 12 hr. had a slight orange tint and melted over the range 35—36·2°. This material was completely removed from the tube, and the second fraction collected during the next 24 hr.; it was very pale yellow, and its melting range was 35·6—36·4°. A third fraction, collected in the same manner, was again very pale yellow, but was contaminated with an unknown impurity which extended the melting range to 32—35·5°. All melting data were obtained at very slow rates of heating, a hot-stage microscope with high magnification and a calibrated thermometer being used. Without these stringent conditions, the difference between the first two fractions (apart from colour) would have been barely detectable, and indeed, under the same conditions several " AnalaR " standard substances rarely showed melting ranges of less than 0·5—1·0°. The second fraction was therefore considered to be very pure and was used in all kinetic and vapour pressure measurements.

Characterisation of the Polymorphs.—The polymorph described by Campbell, Henderson, and Taylor (*loc. cit.*) was readily obtained by cooling to 0° a liquid film of azoxybenzene held between a microscope slide and cover slip. It appeared as well-formed spherulites with brilliant polarisation colours and melted at 29°. This form is now designated III, the stable form being I.

The transformation III ⟶ I occurred at a convenient rate at room temperature, but quantitative measurements with a travelling microscope were eventually abandoned, owing partly to a high degree of spontaneous nucleation, but mainly to the discovery of a further polymorph, designated II, whose transformation to I under thin-film conditions proved much more satisfactory. At a film thickness of 0·02 mm., form II showed a pale brownish-yellow colour under crossed Nicols, in contrast to the brilliantly coloured spherulites of III and the slightly less coloured needles of the stable form I. The final m. p. of II was 36·2°, only 0·2° less than that of the stable form. The transformation II ⟶ I was characterised by a slower rate than the III ⟶ I process, very little spontaneous nucleation, and a well-developed interface between the two forms. Furthermore, during the II ⟶ I transformation, the film became more opaque, and this fact was utilised in developing a photometric method for measuring the rate of the transformation (see below). No reversible transition points were observed and the relationship between the forms in all cases is therefore monotropic.

In view of the slight difference (0·2°) between the m. p.s of forms I and II, further characterisation of II was sought by means of *X*-ray powder photographs, using a Unicam 9-cm. camera with copper K_α radiation. Normally, the powdering of II would have resulted in its transformation to I before a satisfactory photograph could have been obtained. However, with the third fraction of azoxybenzene obtained in the vacuum-distillation, the transformation II ⟶ I was found to be almost completely inhibited, probably owing to some slight impurity, and a powder photograph of II could therefore be obtained. Photographs of I from fractions two and three were identical, while that of II was distinctly different from that of I. Spacings in Å are as follows :

Form I ...	9·01m	5·77w	5·36m	4·65s	3·86s	3·55m	3·22w	3·03m	2·70w	2·29w
Form II ...	8·41m	5·60w	4·58s	4·26s	3·78s	3·17w	3·05m			

(s = strong; m = medium; w = weak)

Density Determinations.—The densities of I and II (fraction three again being used), determined at 20° by flotation in water–sulphuric acid mixtures, were found to be 1·260 and 1·251, respectively.

Establishment of the Linearity with Time of the II ⟶ I *Transformation.*—In view of the higher density of form I, a small contraction away from the II—I interface may occur during the transformation, leading to a fall in rate with time (cf. Hartshorne *et al.*, *J.*, 1935, 1860; *J.*, 1938, 1636). A method of ascertaining whether or not the transformation remained linear with time was therefore necessary. A film of form II, 25 × 37 mm. and 0·025 mm. thick, was prepared between two microscope slides and seeded along one long edge with form I by scratching with a sharp point and painting with a slurry of form I in ethanol. Experiment showed that the use of this slurry had no effect on the transformation other than ensuring complete nucleation along the whole front. The film was kept at constant room temperature in diffused artificial light and photographed at 15-min. intervals, after which the negatives were projected with approximately 15-fold enlargement on to graph paper, and the successive II—I interfaces traced. The areas of transformation obtained in equal intervals of time for a fixed width of interface were cut out with a razor blade and weighed. Since the graph paper was of uniform weight per unit area, a relative measure of the rate of transformation was obtained from the weights of paper cut out. For two films, the transformation was found to be strictly linear with time.

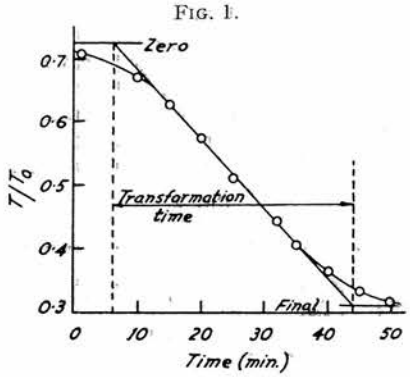
Effect of Film Thickness.—A film was prepared as above with the addition that at one end the microscope slides were held apart with a piece of copper foil, thus producing a wedge shaped film varying from 0·002 to 0·095 mm. in thickness at right angles to the direction of growth, but of uniform thickness along any line parallel to the direction of growth. The transformation was photographed and traced on uniform graph paper as before. This tracing was then divided into three sections of equal width across the direction of growth, each section representing a different average film thickness, and the areas of transformation were cut out and weighed. All three sections showed the same constant rate of transformation. Furthermore, no correlation was ever found between film thickness and transformation rate as measured by the Spekker method described below.

Spekker Absorptiometer Method for measuring Transformation Rates.—Consider a rectangular film of azoxybenzene form II of uniform thickness and area a supported between glass slides. If the film is completely immersed in and at right angles to a uniform light beam of intensity I_0 per unit cross-section area and of total area a_0 ($a_0 > a$), then the total amount of transmitted light is

$$T = I_0(a_0 - a) + I_2 a - K$$

where I_2 is the intensity of the beam transmitted through unit area of the film, and the constant K allows for the light absorbed and scattered by the glass support. This equation may be simplified to $T = \text{const.} - a(I_0 - I_2)$. Let this film now be seeded along one edge with form I, and after times t' and t'' let areas a' and a'' respectively have been transformed to the

FIG. 1.



stable modification. Let I_1 be the intensity of the light transmitted by unit area of form I, and the total light transmitted at t' and t'' be T' and T'', respectively. Then

$$T' = \text{const.} - a'(I_0 - I_1) - (a - a')(I_0 - I_2)$$

and

$$T'' = \text{const.} - a''(I_0 - I_1) - (a - a'')(I_0 - I_2)$$

The rate of change of total light transmitted is

$$(T'' - T')/(t'' - t') = (a'' - a')(I_1 - I_2)/(t'' - t')$$

and is therefore a measure of the rate of change of area transformed. The latter, it should be noted, is a measure of the linear rate of advance of the interface only if the film is of uniform width perpendicular to the direction of growth, and provided no further nucleation occurs. Oblique growth of form I from " dark " regions of the film into the light beam would constitute further nucleation from the point of view of the theory. This was eliminated by having the film completely bathed in the beam in a lateral direction, and by the fact that spontaneous nucleation either along the edges or within the body of the film rarely occurred.

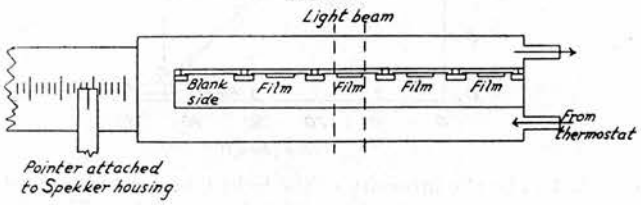
In using the Spekker instrument for rate measurements, it was balanced in the normal way with the solution position occupied by the transforming film, and the solvent position by a microscope slide. Thus at times t' and t'', values of T'/T_0 and T''/T_0 respectively were obtained by inverting the antilog of the drum reading, T_0 being the light transmitted by the blank slide. The rate of change of T/T_0 is $(a'' - a')(I_1 - I_2)/\{(t'' - t')T_0\}$ and is therefore directly proportional to the rate of transformation. Since the latter is constant at a given temperature, the plot of T/T_0 against time is a straight line, the gradient being proportional to the rate. A difficulty arises, however, if all the films do not have the same thickness, for this leads to variation in I_1 and I_2, and the rate of change of light transmitted would vary from film to film even although the actual rate of transformation was the same for each. Furthermore, owing to irregularities in the advancing front, the whole of the front does not enter or leave the beam simultaneously and causes the T/T_0–time graph to be curved at the beginning and end of the measurements. These troubles were eliminated by extrapolating the central linear portion of the graph to the zero and final values of T/T_0 (see Fig. 1). The latter can easily be measured if the direction of growth is vertical and the film extends a few mm. above and below the vertical limits of the beam. From the extrapolation, the time required for that part of the film totally immersed in the light beam to be transformed completely is obtained.

A further requirement is that the light beam should be of uniform intensity along the direction of growth, otherwise a linear rate of transformation would not result in a linear change in the amount of light transmitted. Since photographs showed the Spekker beam to be of uniform intensity along its vertical axis in the slide position, experiments were always carried out so that the front advanced from the bottom to the top of the beam.

Preparation of Films and Measurement of Rates of Transformation.—Films of form II were prepared between microscope slides and cover slides 25 mm. long by 11 mm. wide, the corresponding light beam dimensions being 14 × 12 mm. The measured transformation times therefore corresponded to a 14-mm. advance of interface and a transformed area of 14 × 11 mm.^{2}. Under red-light conditions, a small quantity of powdered azoxybenzene was

melted between a slide and cover slip at 40° on an electrically heated aluminium block, care being taken to exclude air bubbles. The slide was then cooled for 5 min. on a plane horizontal brass surface kept by thermostat at 20°, after which the film of supercooled liquid was seeded along its lower 11 mm. edge with form II. Complete crystallisation occurred in less than 2 sec. By using the same volume of powder (as judged by eye), films were readily obtained, with practice, having uniform thickness within the range 0·02—0·1 mm., for which, as shown above, the rate is independent of thickness. Since prolonged heating at 40° caused some increase in rate, the heating was limited to 1·5 min. for a first melt and 0·5 min. for a second. Only first and second melts were used in the quantitative work, even although no detectable increase in rate occurred after three melts. The same lower edge was now scratched with a sharp point and painted with a slurry of form I in ethanol. Occasionally, transformation of the slight crust

FIG. 2.



along the vertical sides of the film was more rapid than transformation within the body of the film, causing side nucleation and therefore non-linear plots of T/T_0 against time. This tendency was minimised by terminating the scratch 1 mm. from each end of the edge. This procedure for preparing films had to be rigidly adhered to, otherwise considerable variation in rate occurred. Even so, rates varied appreciably from one preparation to another, and accordingly a single middle fraction was used in all measurements.

The films were now transferred to the inner compartment of the double Perspex box shown in plan in Fig. 2. This box was mounted on a brass slide of the same cross-section as that which normally carried the cell-holder, and thus with the aid of the pointer and scale any one of the four films or the blank slide could be positioned accurately in the light beam. Experiments were carried out at 5° intervals between 0° and 30°, water or an ethylene glycol–water mixture being used as thermostat fluid. For measurements at or below 10°, the Spekker instrument was totally enclosed within a dry box provided with suitable windows and port-holes. Measurements below 0° were impossible owing to cracking of the films, and above 30° owing to nucleation difficulties. Red filters (Hilger No. 603) were used on the Spekker absorptiometer so that no wave-length shorter than 6000 Å reached the films.

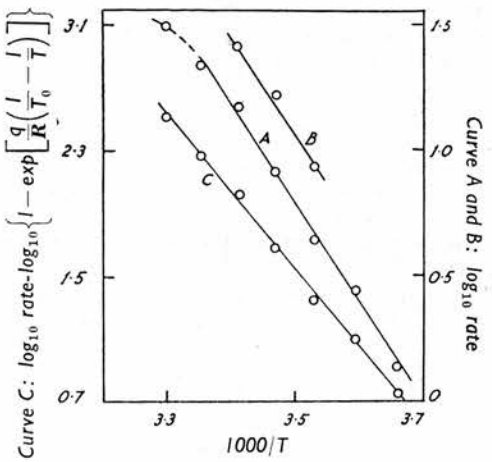
Results for Measurements in Red Light.—The results for a typical exeriment at 25° are given in Fig. 1 and show that the requirements of the theory given above were adequately fulfilled. In the Table are given the arithmetic mean rates, expressed as $10^3 \times$ (transformation time in min.)$^{-1}$, together with the number of experiments on which the mean is based, the standard deviation, and the coefficient of variation. The graph of $\log_{10}$ (Rate) against the $1/T$ is given in Fig. 3, line A. By statistical calculation using regression equations (Weatherburn, " First Course in Mathematical Statistics," Cambridge Univ. Press, 1945) and omitting the 30° point, the equation for A was shown to be $\log_{10}$ (Rate) $= -3932/T + 14{\cdot}55$, from which an apparent activation energy of 17·9 kcal. (standard deviation 0·45) was obtained on the assumption (see p.) that the rate of the transformation can be represented by an Arrhenius-type equation. The 30° point was omitted from the calculation because it was shown to lie more than three standard deviations below the calculated line through the other six points, thus indicating a slight curvature at the high-temperature end of A.

Rates of transformation.

Temp.	0°	5°	10°	15°	20°	25°	30°
			Red light conditions				
Rate	1·390	2·778	4·422	8·180	14·80	21·89	31·33
No. of expts.	16	14	12	19	28	27	22
Standard deviation (S)	0·124	0·181	0·358	0·532	2·74	5·10	3·57
Coeff. of variation (S/Rate)	0·089	0·065	0·081	0·065	0·185	0·233	0·114
			After pre-irradiation with ultra-violet light.				
Rate	—	—	8·49	16·44	25·55	—	—
No. of expts.	—	—	12	18	15	—	—
Standard deviation (S)	—	—	0·855	1·67	3·44	—	—
Coeff. of variation (S/Rate)	—	—	0·101	0·102	0·135	—	—

Influence of Pre-irradiation with Ultra-violet Light on Rate of Transformation.—Variations in rate up to 100% in the early stages of the work were found to be due to exposure of the films (prepared under otherwise standard conditions) to bright daylight. Semi-quantitative experiments at 20° showed that irradiation of form II films with a Hanovia ultra-violet lamp at a distance of 30 cm. before seeding with form I, followed by transformation in red light, gave increased rates up to *ca.* 100% after 5 minutes' irradiation, with no further increase up to 10 minutes' irradiation. On re-melting and re-transformation of the films without further irradiation, the rates tended to return to normal red-light values. This tendency was greater the shorter the period of irradiation. If the irradiation was carried out with the films in the liquid state (*i.e.*, before being seeded with form II), 10 seconds' exposure was sufficient to cause the maximum increase in rate (again *ca.* 100%). In this case the effect was more permanent, several re-melts and re-transformations being necessary before any noticeable decrease in rate

FIG. 3.



occurred. Quantitative measurements were carried out at 10°, 15°, and 20°, the films being prepared in the same manner as for the red-light work, with the addition of 15 seconds' irradiation before seeding with the metastable form. Experiments below 10° were impossible owing to cracking of the films on cooling, and above 20° owing to difficulty of securing complete nucleation with form I at all points simultaneously along the lower edge of the films. Results are given in the Table and plotted in Fig. 3, line *B*. In view of the small number of points, little confidence can be attached to the slope of line *B*, but the indication is that no change in apparent activation energy occurs after irradiation.

Temperature Rise at the II–I *Interface during Transformation.*—Calculated by Hartshorne and Roberts's procedure (*J.*, 1951, 1097), the temperature rise at the interface was found to be of the order 0·03°, reasonable values for the specific heat and thermal conductivity of azoxybenzene being assumed by comparison with other organic compounds. This rise is very little more than the variation in the temperature of the thermostated Perspex box, and would have no significant effect on the rate measurements.

Vapour-pressure Measurements and Heat of Sublimation of Form I.—Vapour pressures were determined by Knudsen's effusion method (*Ann. Physik*, 1909, **29**, 179), a cylindrical brass effusion cell closed with a platinum foil diaphragm soldered to a screw-on lid being used. The construction was such that the azoxybenzene was contained within a perfect cylindrical volume 9·52 mm. long and of 4·76 mm. radius, the axially placed orifice in the 0·014-mm. thick platinum foil being 0·905 mm. in radius. During effusion in a vacuum better than 5×10^{-6} mm., the cell was contained in a vertical copper tube, 3″ long by 1″ in diameter, fused at the upper end to a B34 Pyrex joint and closed at the lower end by a copper disc brazed on to the tube. The lower end of the tube contained a Wood's metal plug fused to the copper and having a cylindrical recess which was a close fit to the effusion cell. The latter was thus in good thermal contact with the water thermostat surrounding the copper tube, the top of which was 2″ below the surface of the water. The minimum distance between the cell and the cold surface of a liquid-oxygen trap connected to the Pyrex joint was 8″. The same material (well ground) being used as for the kinetic measurements, effusion was carried out at the desired temperature for several hours before the first weighing of the cell. Thereafter, five successive weighings were carried out after effusion for intervals of 400—3000 min. depending upon the vapour pressure, the loss

in weight in any intervals being 10—30 mg. After the pumps had been switched on, 5 min. elapsed before the commencement of the timing of any interval to allow the pressure to fall to $<10^{-3}$ mm. Calculated in the usual manner, the five values of the vapour pressure at any one temperature did not differ by more than a few units % from the arithmetic mean value. By Whitman's method (*J. Chem. Phys.*, 1952, **20**, 161), the above cell dimension being used, the probability factor W for the cell was found to be 0·959. Theoretically this value of W is applicable only when the cell contains a very thin layer of solid on the bottom, and if the cell initially contains an appreciable quantity of solid, the vapour pressure should show an apparent decrease as the cell is emptied. In practice, no systematic variation was ever observed, indicating that under the present conditions the depth of solid in the cell was not an important factor. An alternative derivation of W (Bradley and Volans, *Proc. Roy. Soc.*, 1953, *A*, **217**, 515; Rossman and Yarwood, *J. Chem. Phys.*, 1953, **21**, 1406) gave a value between 0·95 and 1·0, depending on the values assumed for the evaporation coefficient and the effective area of the solid in the effusion cell. From a practical point of view, therefore, errors due to the use of the Whitman figures would not be more than a few units % and would have very little influence on the slope of the $\log_{10} p$–$1/T$ graph. Results were as follows :

Temp.	19·2°	23·2°	27·2°	31·2°	35·2°
Vapour pressure $\times 10^4$, mm. Hg	0·735	1·26	2·11	3·71	6·08

Calculation by use of regression equations showed that the vapour pressure (in mm.) can be represented by $\log_{10} p = -5201/T + 13{\cdot}66$, which leads to 23·7 kcal./mole for the heat of sublimation, with a standard deviation of 0·3 kcal.

To check the accuracy of the measurements, the vapour pressure of benzophenone (for which accurate values are known; Neumann and Völker, *Z. physikal. Chem.*, 1932, *A*, **161**, 33; Hartshorne and Bradley, personal communication) was determined over the same pressure range. The material used (B.D.H.) was crystallised from ethanol followed by vacuum-sublimation as for azoxybenzene, and had a melting range 47·9—48·2°. The measured vapour pressures, together with Neumann and Völker's values, were as follows :

Temp.	9·0°	17·0°	21·4°	25·3°
Observed v. p. $\times 10^4$ (mm. Hg)	0·74	2·24	3·92	6·04
Neumann's value $\times 10^4$ (mm. Hg)	0·71 *	2·14	3·89	6·46

* Extrapolated value.

The discrepancies are considered to be slightly greater than the experimental error, and indicate that the value of W should be a few units % higher than the Whitman figure in order to reduce the lower values, and that slight self-cooling occurred at the highest pressure. By using an effusion cell of the same dimensions but smaller orifice (radius 0·518 mm., Whitman W 0·976) the vapour pressure at 25·3° was found to be $6{\cdot}51 \times 10^{-4}$ mm., which supports the suggestion of self-cooling at this pressure with the larger-orifice cell. However, if the above results are used to calibrate the larger-orifice cell, the corrected azoxybenzene values lead to a heat of sublimation not greater than 24·9 kcal./mole, only 1·2 kcal./mole greater than that obtained when using the Whitman value of W. The heat of sublimation can therefore be given with confidence as 24 ± 1 kcal./mole. Measurements on liquid azoxybenzene between 37° and 49° gave $\log_{10} p$ (mm. Hg) $= -4361/T + 10{\cdot}97$, corresponding to a heat of vaporisation of 19·9 kcal./mole (standard deviation 0·13), and therefore a heat of fusion of *ca.* 4 kcal./mole.

Discussion

Transformation under Red-light Conditions.—The transformation form II ⟶ form I, in view of its strict linearity with time, independence of film thickness, and the occurrence of only slight spontaneous nucleation, has proved very satisfactory for kinetic measurements near room temperature under thin-film conditions. The average coefficient of variation of the rate is 11·7% (*i.e.*, on the basis of a rate = 100), a comparable figure in the sulphur work (Hartshorne, personal communication) being 11%, and can be considered good for this type of kinetic work. The low variance is considered to be due to (*a*) the high purity of the azoxybenzene, (*b*) the carefully standardised procedure for preparing and transforming the films, and (*c*) the fact that the total area of transformation at any one temperature was relatively large (about 30 cm.^{2} as compared with about 4·5 cm.^{2} for sulphur). Reasonable confidence can therefore be placed in the activation energy and pre-exponential factor derived from the rate measurements.

On the basis of an Arrhenius-type equation, the apparent activation energy is

17·9 kcal./mole (Fig. 3, line *A*). This is significantly less than the heat of sublimation of form II, *viz.*, 23 ± 1 kcal./mole, obtained on the reasonable assumption of 1 kcal./mole for the heat (q) of the transition II ⟶ I : cf. $q = 0{\cdot}7$, 1·4, and 1·5 kcal./mole for benzophenone, carbon tetrabromide, and *n*-undecane respectively (Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier, 1950). However, the indicated curvature at the high-temperature end of line *A* suggests that the expected maximum in the rate (observed with sulphur) might have been realised had it been possible to carry out rate measurements at temperatures nearer the theoretical transition point (T_0), which occurs above the m. p. of either form and where the rate of transformation would be zero. In view of the closeness of the m. p.s of the two forms, T_0 would probably occur at a temperature not higher than about 50°. An estimate of T_0 can be obtained as follows, the units of the vapour pressure p being mm. Hg. The equation for the solid–vapour curve of form I is $\log_{10} p = -5201/T + 13{\cdot}66$, and if it is assumed that $q = 1$ kcal./mole, the corresponding equation for form II is therefore $\log_{10} p = -4976/T +$ constant. The vapour pressure of form II at its m. p. (36·2°) can be obtained from $\log_{10} p = -4361/T + 10{\cdot}97$, the equation for the liquid–vapour curve, and hence the value of the constant found to be 12·95. The two solid–vapour curves can now be shown to intersect at 44°, which is the value of T_0. This value, in view of the small value of q, is subject to appreciable error, but the calculation does show that $q = 1$ kcal./mole is consistent with a value of T_0 between 40° and 50°. It is of interest therefore to consider the results for the present monotropic process in the light of the mechanism proposed by Hartshorne for the enantiotropic sulphur transformation. The latter is based on the difference in rates of escape of molecules from the two adjacent lattices and leads to the equation

$$\log_e \text{Rate} - \log_e\{1 - \exp[q(1/T_0 - 1/T)/\boldsymbol{R}]\} = -E/\boldsymbol{R}T + \log_e \tfrac{1}{2}A$$

where E and A are respectively the activation energy of escape and the temperature-independent factor of the rate of escape of molecules from the metastable lattice. In the case of sulphur, the plot of the left-hand side of the equation against $1/T$ did not give the required straight line except in the temperature range 0—30°, the corresponding value of E being close to 22·5 kcal./mole, which is the accepted value of the heat of sublimation of monoclinic sulphur. Hartshorne has shown, however, that over the whole range of measurements (0—80°) the deviations from the requirements of the theory can be accounted for by quite small variations in the activation energy of escape of molecules from the stable lattice. Applied to the present results, with $q = 1$ kcal./mole and $T_0 = 50°$ C, the above equation gives line *C* in Fig. 3, the slope coresponding to $E = 22{\cdot}5$ kcal./mole, which agrees well with 23 ± 1 kcal./mole, the heat of sublimation of form II. Variation of q from 0·5 to 2·0 kcal./mole or of T_0 from 50° to 40° C does not alter the value of E by more than 1 kcal. or substantially affect the fit of the points to a straight line. The value of A, calculated at 20°, is $7{\cdot}72 \times 10^{14}$. Theoretically, if application of Hartshorne's equation does in fact yield a straight line for *C* in Fig. 3, then line *A* should be slightly curved over its entire length. The curvature required (found by mathematical transformation of *C* back to *A*) is, however, very slight and the resulting curve is indistinguishable within the experimental error from the straight line *A*. Over a larger temperature range, the curvature would probably be more apparent as it is with sulphur. The same conclusion regarding activation energy was reached by Hartshorne *et al.* for *o*-nitroaniline (*J.*, 1935, 1860), but not for mercuric iodide (*J.*, 1938, 1636) where the activation energy was less than the heat of sublimation.

Calculations based on work by Burgers (*Proc. K. Ned. Akad. Wet.*, 1947, **50**, 719) and Mott (*Proc. Phys. Soc.*, 1948, **60**, 391) have shown (Hartshorne, *Discuss. Faraday Soc.*, 1949, **5**, 149) that for sulphur the thermal activation of one molecule with energy equivalent to the heat of sublimation leads to the transformation of *ca.* 10^7 molecules. By the same procedure, with use of the above value of A, or by application of the Polanyi–Wigner equation, the results for azoxybenzene give a value of *ca.* 10^9. This number of molecules corresponds to a unit of volume of *ca.* 3×10^{-13} cm.^{3}, which is within the range of the estimated size of a mosaic block. Hartshorne (*loc. cit.*; cf. Garner, *ibid.*, p. 194) has interpreted this behaviour on the basis of a mosaic block theory. It is thought that the transformation occurs with low energy of activation over small elements of volume (*i.e.*,

mosaic blocks) and that a much higher energy is required to " bridge " adjacent blocks. If the bridges are formed by condensation of molecules from the vapour phase, the higher energy of activation will be approximately equal to the heat of sublimation and will determine the temperature coefficient of the transformation.

Further parallels to the sulphur transformation are as follows: (*a*) although the average rate of interface advance was constant under given conditions, microscopic examination showed that the transformation proceeded spasmodically over short distances, caused no doubt by lattice discontinuities of one kind or another, and that growing stable crystals did not change their orientation when crossing boundaries between differently oriented metastable crystals; (*b*) an estimate by Hartshorne's method (*J.*, 1951, 1113) of the vibration frequency of molecules from which bridges between mosaic blocks are formed was 10^5—10^6 times greater at 20° than the usual frequency of *ca.* 10^{13} sec.$^{-1}$ (with sulphur the discrepancy at 0° is 10^4 times); (*c*) from the vapour-pressure data, the rate of evaporation at 20° can be shown to be 10^5—10^6 times greater than that calculated from the Polanyi–Wigner equation: the corresponding discrepancy for rhombic sulphur is *ca.* 10^4 (*loc. cit.*).

Transformation after Irradiation with Ultra-violet Light.—The approximate doubling of the rate of the II ⟶ I transformation after irradiation with ultra-violet light could be due to either a reduction in the activation energy of *ca.* 500 cal./mole, a quantity which is too small to be detected in the present instance (cf. Fig. 3) or an approximate doubling of the effective volume of the mosaic blocks. The fact that the increase in rate is more pronounced when irradiation is carried out with the films in the liquid rather than the solid state, suggests that the primary cause is a photochemical one. Since it is known (Badger and Buttery, *loc. cit.*) that irradiation by sunlight of azoxybenzene in organic solvents slowly leads to the formation of *o*-hydroxyazobenzene, it seems likely that minute amounts of this compound would be produced during the 15-sec. ultra-violet irradiation. Incorporation of the hydroxy-compound in the lattice of form II may then have been such as to influence the physical state of the films and favour the bridging of lattice discontinuities. In this connection, it has been observed that (*a*) red-light films, after being " annealed " at room temperature in the dark for 18 hr., were transformed at a much slower rate than normal, and (*b*) if the transition III ⟶ II preceded the II ⟶ I process in an otherwise standard red-light film, the II ⟶ I rate was much greater than normal. Both observations show that the physical state of the films had an important influence on the rate of transformation. However, attempts to reproduce the acceleration effect with known mixtures of azoxybenzene with *o*-hydroxyazobenzene failed. The destruction of the effect on frequent remelting of the films suggests, on the other hand, that the active photochemical product may be *cis*-azoxybenzene, which would revert to the normal form on melting (cf. *cis*-azo-compounds; Campbell, Henderson, and Taylor, *J.*, 1953, 1281). However, the existence of *cis*-azoxybenzene has not yet been established unambiguously (Gehrckens and Müller, *Annalen*, 1933, **500**, 296).

Grateful acknowledgments are made to the D.S.I.R. for the award of a maintenance grant (to A. H.), and to Dr. N. H. Hartshorne and Dr. R. S. Bradley for discussions.

UNIVERSITY OF EDINBURGH. [*Received, October 8th*, 1954.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

Preprinted from the Journal of the Chemical Society, March, 1955, (5803), pages 1033—1034.

The Thermal Decomposition of Ammonium Dichromate.

By DUNCAN TAYLOR.

[Reprint Order No. 5803.]

FOR the thermal decomposition of ammonium dichromate with continuous evacuation in the temperature range 188—218°, Fischbeck and Springler (*Z. anorg. Chem.*, 1939, **241**, 209) reported that after an induction period t' the fraction decomposed at any time t is proportional to $(t - t')^4$, up to about 30% decomposition (approximately the maximum-rate stage), as required by a linear growth of spherical nuclei whose number increases linearly with time. From about 30 to 100% decomposition, a contracting-sphere type of mechanism applied, governed by the equation $1 - (1 - x)^{\frac{1}{3}} = \text{const.}\ (t - t_0)$, where x is the fraction decomposed, and t_0 is the time at which the maximum rate occurred. Reinvestigation of the decomposition without employing continuous evacuation has revealed new features of the kinetics, and an alternative mechanism is proposed.

Experimental and Results.—Decompositions were carried out at 195—218° in an apparatus similar to that of Garner and Haycock (*Proc. Roy. Soc.*, 1952, *A*, **211**, 338) with the addition, between the reaction vessel and expansion bulbs, of a trap (P_2O_5) to remove water vapour. The pressure of the remaining nitrogen was measured with a Macleod gauge placed after the expansion bulbs. The reaction-vessel temperature was controlled within ±0·05° by an electric furnace and electronic relay, and was measured with a Pallador thermocouple, which was calibrated against a platinum resistance thermometer. Small crystals (0·1—0·2 mm.) of ammonium dichromate, obtained by rapid crystallisation of " AnalaR " material at 30—40°, were used in 5—14 mg. quantities in a closed vessel constructed from 2 cm.² of 0·025-mm. thick platinum foil. The thermocouple indicated a maximum heating-up period of about 5 min., and gave no evidence of self-heating of the crystals during decomposition. Before decomposition, samples were degassed for 3—4 hr. at room temperature and a pressure less than 10^{-5} mm., no significant difference in rates being observed with 18 hours' evacuation. The total volume of the system was 6200 c.c.

Typical pressure–time curves are given in Fig. 1, zero time being the moment when the sample reached the hot zone of the reaction vessel. The maximum rate in the autocatalytic stage occurred in all cases at about 20% decomposition, calculated on the basis of the scheme, $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3,H_2O + 3H_2O + N_2$ (Fischbeck and Springler, *Z. anorg. Chem.*, **1938**, **235**, 183), and had a temperature coefficient corresponding to an energy of activation of 33 kcal./mole (see Fig. 2, line *A*). Irrespective of temperature, this stage was complete after about 45% decomposition, and was followed by a constant-rate stage over the range 45—65% decomposition, with an energy of activation of 38 kcal./mole (see Fig. 2, line *B*). Both the maximum rate and the constant rate were directly proportional to the initial weight of the sample and were reproducible to within 10%. Following the constant-rate process, the pressure increased in an irregular manner and, depending on the temperature, the maximum decomposition even after several days' heating was only 75—85%. Induction periods (defined as the time required for the pressure to reach 10^{-3} mm.) varied from 2 to 15 min., but in general decreased with increasing temperature. Slight grinding of the crystals did not significantly alter the rates at any stage, but prolonged grinding resulted in the disappearance of the induction period and in increased irreproducible rates, the maximum of which occurred very early.

Discussion.—The results differ from those of Fischbeck and Springler in the following respects: (*a*) the occurrence of the maximum rate earlier in the decomposition; (*b*) the occurrence of a constant-rate stage, indicating a linear interface reaction (cf. Jacobs and Tompkins, *Proc. Roy. Soc.*, 1952, *A*, **215**, 273); and (*c*) failure to attain 100% decomposition at any temperature. Furthermore, it has been found that for the initial stages of the decomposition the equation $x = (t - t')^n$ fits the present results only approximately, n varying between 2 and 3, and that the equation of the contracting-sphere mechanism fits moderately well only from

45 to 70% decomposition, the corresponding energy of activation being about 35 kcal./mole, in contrast to 49 kcal./mole found by Fischbeck and Springler. These differences are thought not to be due to the different experimental conditions because (*a*) in both cases the pressure of residual water vapour is estimated to be $<10^{-4}$ mm., and (*b*) experiment showed that the decomposition of single crystals (about 8 mg.) was unaffected by the presence initially of 0·06 mm. pressure of nitrogen.

The autocatalytic stage can best be represented by the Prout–Tompkins equation, $\log_{10} p/(p_f - p) = \text{constant} + k \log_{10} t$ (*Trans. Faraday Soc.*, 1944, **40**, 488; 1946, **42**, 468), with a single value of k instead of the usual two values, when the final pressure p_f (estimated by trial and error) corresponds to the conclusion of the stage (see Fig. 2, line *C*). The use of the experimental

FIG. 1.

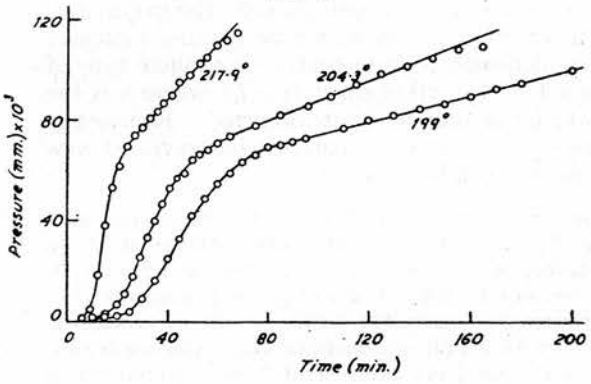
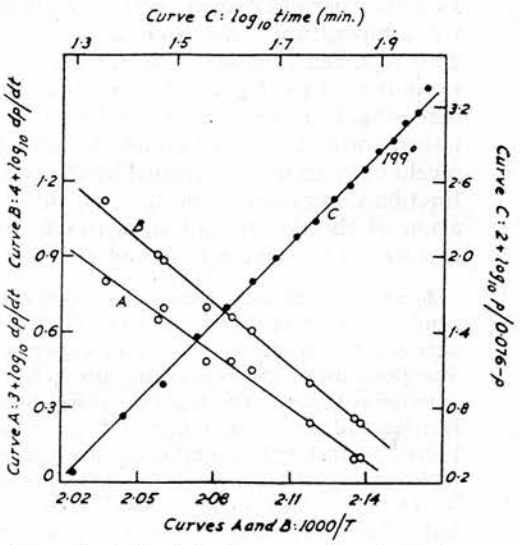


FIG. 2.



pressures in the equation involves the assumption either that the interface reaction is insignificant during the autocatalytic stage, or that the pressure due to the latter process at any time is a constant fraction of the total. The agreement of the results with the equation is in keeping with the fact that during decomposition the ammonium dichromate lattice probably undergoes changes (as judged from the lattice dimensions of dichromate and chromic oxide) similar to those for permanganates, for whose decomposition the Prout–Tompkins mechanism was originally proposed. The need for a single value of k is unusual, but may be due to the completion of the autocatalytic stage at only about 45% decomposition. The fit of the equation was less satisfactory if allowance was made for the short induction periods, and furthermore, although the maximum rate varied regularly with temperature (see Fig. 2, line *A*), the variation of k with temperature was erratic. For the first 5% of the decomposition, the equation did not apply satisfactorily, and this fact taken in conjunction with the occurrence of induction periods suggests that a nucleation process may precede the autocatalytic stage.

UNIVERSITY OF EDINBURGH.

[*Received, October* 14*th*, 1954.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

Reprinted from the *Transactions of the Faraday Society*, No. 286,
Vol. XLII, Parts 3 and 4, March–April, 1946.

THE OXYGEN ABSORPTION OF RUBBER VULCANISATES IN LIGHT.

THE OXYGEN ABSORPTION OF RUBBER VULCANISATES IN LIGHT.

By S. Horrobin, R. G. A. New and D. Taylor.

Received 23rd August, 1945.

The investigations described in this paper arose from some earlier observations in these laboratories of the effect of light on the rate of oxygen absorption by vulcanised rubber which were made by Morgan and Naunton [1] during a study which was mainly concerned with the reaction in the dark. These authors had shown that the rate of oxygen absorption, in the dark, of a rubber vulcanised with diphenylguanidine as accelerator, without and with addition of dimethoxydiphenylamine as antioxidant obeyed the Arrhenius equation up to 80° C. If the samples had been exposed to light immediately before the measurements commenced, an increased rate of oxygen absorption was observed, which persisted for some time in the dark.

An autocatalytic reaction, with a chain mechanism, was postulated, with the following steps :

(i) a thermal activation of rubber double bonds

$$R \rightleftharpoons R^* \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(ii) a (rapid) addition of oxygen to the activated bonds

$$R^* + O_2 \rightarrow RO_2^* \quad . \quad . \quad . \quad . \quad (2)$$

(iii) reaction of the activated peroxide with another double bond

$$RO_2^* + R \rightarrow RO_2 + R^* \quad . \quad . \quad . \quad (3)$$

so continuing the chain.

(iv) deactivation

$$(a)\ RO_2^* \rightarrow RO_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$(b)\ RO_2^* + i \rightarrow \text{deactivated products} \quad . \quad . \quad (5)$$

where i represents antioxidant.

The effect of light was explained by the introduction of a second activation process

(v) $$R + h\nu \rightarrow R^*. \quad . \quad . \quad . \quad . \quad (6)$$

On this postulate, light would have no other effect on the mechanism, and the curves of rate of oxygen absorption versus time would be of the same form as in the dark.

The work which was then planned was designed to permit the measurement of the rate of oxygen absorption of a specimen uniformly illuminated with light of known wavelength and intensity, and to study in greater detail the effects of degree of vulcanisation, of concentration of antioxidant, and of acetone extraction.

The results which are now described represent the first, largely exploratory, phase of this larger investigation.

[1] Morgan and Naunton, *Proceedings of the Rubber Technology Conference,* 1938, 599.

The first experiments were carried out with " white " light, but most of the results to be described were obtained using a mercury vapour lamp. The variations of the rate of oxygen absorption with intensity and wavelength of the light and with temperature have not yet been studied, but the results have already shown that the reaction in light is more complex than was postulated above.

Experimental.

The work was carried out in two series, the first at 34° C. providing the results in Figs. 2 and 6, and the second at 25° C., providing all other results. All the rubber samples were in sheet form, about 1 mm. thick, and were exposed as 4 cm. diameter discs in the oxidation apparatus in Fig. 1. The oxidation cell A containing the rubber sample B formed part of the rear section of the lagged stainless steel water jacket C and was closed by the window D held in position by the steel locking ring E. Window F closed the front portion of the water jacket. Water from a thermostat controlled to ± 0·1° C. was pumped through the two sections of the jacket in the manner indicated by the arrows. A steel capillary tube G connected the oxidation cell to capillary tetralin manometers of the Warburg type, one side of which was open to the atmosphere. For the first series of measurements, high intensity illumination was provided by a " white " beam, filtered through 0·5 % copper sulphate solution, from a 500 watt tungsten filament projector lamp, and in the second parallel light from a 125 watt Osira mercury lamp was used. In both cases the optical system was of glass. The mercury lamp was operated from mains stabilised by a Solus stabiliser, and maintained an intensity constant to within ± 5 % as measured on a Weston photocell. In both cases, oxidation rates were roughly equal in magnitude. The use of filters with the mercury lamp led to inconveniently low rates.

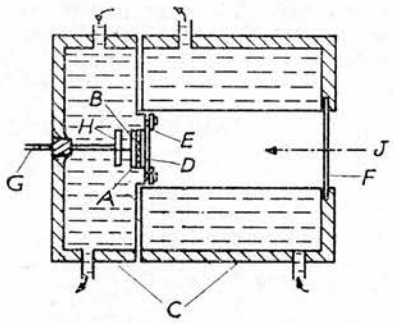


FIG. 1.—Oxidation apparatus.

The experimental procedure was briefly as follows. The rubber sample, stored over nitrogen in the dark since its preparation, was cut to the necessary size in dim light, weighed, introduced into the oxidation cell, and then evacuated for several hours at a pressure less than 0·1 mm. mercury to remove dissolved gases. Oxygen, dried over calcium chloride and stored over mercury, was then admitted to a pressure of one atmosphere, and the system allowed to reach physical equilibrium in the dark (usually overnight). A pressure-time curve was plotted, pressures being measured at constant volume, and from the slope at any point and the measured volume of the apparatus the rate of absorption in g. oxygen/sq. cm. rubber/min. was calculated. By taking simultaneous readings on a tetralin manometer connected to a blank cell H, which had the same free volume as the reaction system, corrections were applied for changes in atmospheric pressure and temperature. Since the total pressure range of the tetralin manometers was only 20 mm. mercury, provision was made for the admission of small quantities of oxygen as the oxidation proceeded. This small pressure range also meant that all rates were measured within a few mm. of atmospheric pressure. The use of tetralin as manometric fluid and the fact that the reaction system volume was only 3 c.c. conferred high sensitivity, rates as low as 10^{-8} g. oxygen/sq.cm./min. being measured without difficulty. No absorption of oxygen by the tetralin

in the manometers could be detected. The percentage light transmission of the samples was measured before (80-90 %) and after (60-70 %) exposure with the aid of the photo-cell and the absorption rates then corrected for 100 % absorption, allowing for 50 % back reflection into the sample of the transmitted light, and assuming direct proportionality between rate and light intensity. This correction is rather arbitrary and was not applied to pale crepe samples owing to their low absorption. In practically all cases, the increase in weight of the rubber after exposure agreed closely with the oxygen consumption as calculated from the rate-time curve.

All the vulcanisates had the composition crepe rubber 100 parts (by weight), zinc oxide 2·5, sulphur 3, diphenylguanidine 1·5, and were cured at 141° C. In the first series, the curing time was 60 minutes, and in the second 10, 45 and 180 minutes as required. The antioxidants were used at a concentration of 1 part by weight except in the series where the proportion was varied. Several antioxidants were used, with closely similar results. For the most part, the antioxidant was Neozone A (N-phenyl-α-naphthylamine) or Neozone D (N-phenyl-β-naphthylamine). The crepe samples were unmilled. The results are shown in Figs. 2-8 which are self-explanatory. Dark rates were measured only in the first series at 34° C. In the second series at 25° C. the dark rate was too low to measure. The time zero for all experiments in the light was taken as the point when illumination commenced. Reproducibility of results to better than 10 % was obtained only when the samples concerned were from the same sheet and differed in age since the time of vulcanisation

TABLE I.—Tensile Strength Measurements.

	10 min.	45 min. (normal).	180 min.
Wt. O_2 absorbed in mg./cm.^{2} .	0·05	0·1	0·23
% O_2 absorbed . . .	0·195	0·503	1·12
% drop in tensile strength .	16	14	12·5

by not more than 2-3 weeks. With larger differences in age, while the form and relative positions of the curves remained the same, differences of 30-50 % in the absolute oxidation rates occurred. All the samples in any one set were thus exposed with the minimum possible interval. A series of tensile strength measurements was carried out on the set of samples containing 1 part of antioxidant, cured for varying times, after exposure to the approximate completion of the first "stage" (see Discussion) of the oxidation, three samples being exposed in each case. A specially constructed small dumbbell cutter was used for the tensile tests. Results are given in Table I.

Discussion.

Effect of Diffusion of Oxygen.—Williams and Neal [2] have shown that the rate of oxidation of vulcanised rubber is independent of the oxygen pressure, and therefore of the concentration of dissolved oxygen, down to pressures of 200-300 millimetres of mercury. From this observation, and a knowledge of the permeability of rubber to oxygen, it can be calculated [1] that for the present experimental conditions the concentration of oxygen is maintained by diffusion at all points within a sheet of 1 mm. thickness at a value corresponding to a pressure not less than half an atmosphere. Diffusion would not, therefore, be a rate-controlling step in the oxidation process. Recent work by Carpenter and Twiss [3] has

[2] Williams and Neal, *Ind. Eng. Chem.*, 1930, **22**, 874.
[3] Carpenter and Twiss, *Nature*, 1944, **154**, 673.

shown some reduction in rate on reducing the pressure from 1 to ½ atmosphere. Under our conditions this would not appreciably modify the above conclusions.

The Dark Reaction.—The rate of oxygen absorption in the dark, at 34° C., slowly increased to an approximately constant value. Antioxidants reduced the rate and hastened the attainment of a lower constant value (Fig. 2). The results are in accord with the mechanism postulated by Morgan and Naunton.[1]

The Light Reaction.—All the results in light can be broadly described in terms of three stages :

The First Stage.—The rate of oxygen absorption was initially rapid but quickly fell. This is clearly shown by all the curves for vulcanised rubber, and to a lesser extent by those for pale crepe. This stage occurred only once with each sample. When the light was removed the rate rapidly fell nearly to the dark rate. On re-exposure to light the rate immediately returned to a value not higher than when the light was switched off (Fig. 6). Exposure to light *in vacuo* had no effect on the subsequent rate either in the dark or in light. This stage was not affected by added antioxidants. This is best seen from Fig. 5 where all the set of samples had been compounded and cured together. Comparisons between corresponding samples in other, different sets, *e.g.* Figs. 3 and 4, also show differences no greater than is to be expected from the reproducibility of

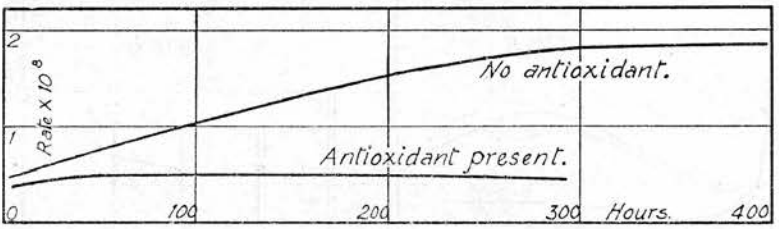


FIG. 2.—Dark rate.

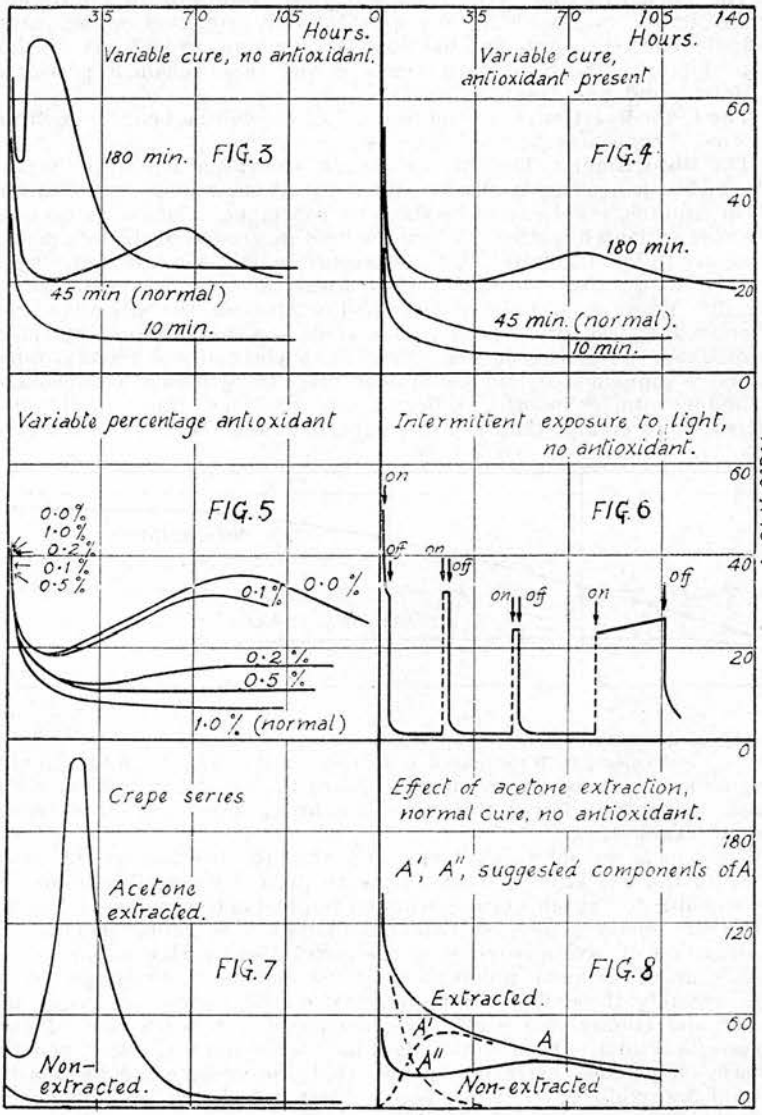
either. The initial rate increased with time of cure (Figs. 3 and 4) and it was markedly increased by acetone extraction (Figs. 7 and 8). The oxygen absorption during this stage had little, if any, effect on tensile strength (Table I).

These facts do not support the view that the reaction at this stage is due to the oxidation of some impurity present in small amount nor that it is due to oxygen vulcanisation on residual active centres. Farmer and others [4] have suggested that the oxidation of rubber commences by formation of hydroperoxides at the *a*-methylene carbon atoms of the isoprene units. A small proportion of these may be specially reactive in light—possibly those adjacent to terminal double bonds—*cf.* Boggs and Blake [5] and Hauser and Sze.[6] The increase in rate with time of cure suggests that adjacent sulphur bridges have an activating effect, and the increase on acetone extraction shows that the acetone soluble matter (natural antioxidant) has a protective effect not shared by added antioxidants.

The Second Stage.—The rate of oxygen absorption, due to the reaction postulated for the first stage, would fall rapidly, to zero. In fact, after the initial rapid fall, the rate either approached a constant value, or passed through a minimum, rising to a maximum. It is suggested that at this stage the experimental curve is the resultant of two reactions,

[4] Farmer, *et al.*, *J.C.S.*, 1942, 139, 513 ; 1943, 125.
[5] Boggs and Blake, *Ind. Eng. Chem.*, 1930, **22**, 744 ; 1934, **26**, 1283.
[6] Hauser and Sze, *J. Physic. Chem.*, 1942, **46**, 124.
[7] Twiss, *Nature*, 1945, **156**, 9.

the second being the autocatalytic reaction, starting at zero rate, postulated by Morgan and Naunton.[1] In view, however, of the work of Farmer and others [4] on hydroperoxide formation, and the greater likelihood, in



a solid system, of a radical and atom chain rather than an energy chain, we should now prefer to substitute equations (1) to (6) by

$$\mathrm{RH} \rightleftharpoons \mathrm{R}— + \mathrm{H}— \quad . \quad . \quad . \quad . \quad . \quad (7)$$
$$\mathrm{R}— + \mathrm{O}_2 \rightarrow \mathrm{RO}_2^- \quad . \quad . \quad . \quad . \quad . \quad (8)$$
$$\mathrm{RO}_2^- + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}— \quad . \quad . \quad . \quad . \quad (9)$$
$$\mathrm{RO}_2^- + \mathrm{H}— \rightarrow \mathrm{ROOH} \quad . \quad . \quad . \quad . \quad . \quad (10)$$
$$\mathrm{RO}_2^- + i \rightarrow \text{other oxidation products} \quad . \quad . \quad (11)$$
$$\mathrm{RH} + h\nu \rightarrow \mathrm{R}— + \mathrm{H}— \quad . \quad . \quad . \quad . \quad (12)$$

where R—, RO_2^-, and H— are radicals and ROOH is a hydroperoxide.

Support for equation (12) is given by J. C. Bateman's observation (7) that small quantities of hydrogen are evolved when rubber is exposed to light *in vacuo*.

This modification does not affect the kinetics. The reaction, on this mechanism, should start at zero rate and rise to a constant rate which may, however, be high. This constant rate is shown by the curves for normal vulcanisates containing antioxidants in normal amounts (Figs. 4 and 5) and also by pale crepe (Fig. 7). It is also shown by samples cured for a short time only (Figs. 3 and 4). Without added antioxidant, and with normal cure (Fig. 3) the rate rose to a maximum and then fell, as would be expected if the " constant " value were so high that the concentration of accessible isoprene units was appreciably reduced before this rate was attained. The area under the curve for extracted crepe (Fig. 7) corresponds to absorption of one oxygen molecule for every eight isoprene units. Prolonged cure led to the appearance of this maximum even in presence of added antioxidant (Fig. 4) and to an earlier and higher maximum in absence of added antioxidant (Fig. 3). Crepe rubber showed a very pronounced maximum (Fig. 7) after removal of the natural antioxidant by acetone extraction, and the curve for acetone extracted vulcanised rubber (Fig. 8) may be interpreted in the same way, as indicated by its resolution into the two broken curves.

The marked effect of vulcanisation may be due to an additional chain propagating reaction involving adjacent sulphur bridges :

$$RO_2^{\cdot} + \text{—S—S—} \rightarrow R\text{—} + \text{—S—}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{—} \quad . \quad . \quad . \quad (13)$$

The Third Stage.—The curves which showed a maximum then fell, but except for pale crepe (Fig. 7) they did not approach a zero rate as would be expected if all the accessible isoprene units were being consumed and no other reaction were taking place. Instead, they approached a constant value at a fairly high level (Figs. 3 and 4). It is suggested that this stage is concerned with the subsequent action, as an oxidising agent, of the hydroperoxide produced in the second stage, leading to products which are capable of oxidising still further by absorption of more oxygen.

Summary.

The oxygen absorption of rubber vulcanisates in light shows in succession (i) a rapid initial rate, rapidly falling, (ii) a constant rate or a rate rising to a maximum and falling (iii) to a nearly constant rate. All the rates are much higher than those in the dark at the same temperature. In stage (i), added antioxidants have no effect, the rate increases with time of cure, and on acetone extraction. In stage (ii) the rise to a maximum is most pronounced in absence of antioxidants and with prolonged cure. It is depressed by increase in antioxidant concentration or by reduction in time of cure until this stage merely appears as a constant rate after (i). The mechanism of these stages is discussed.

The authors wish to express their indebtedness to Professors E. K. Rideal, F.R.S., and C. N. Hinshelwood, F.R.S., for valuable discussions during the course of this work, as well as to colleagues in the Research Department, and to Dr. W. J. S. Naunton and the Rubber Service Department for advice and for the preparation of the samples and the tensile strength measurements.

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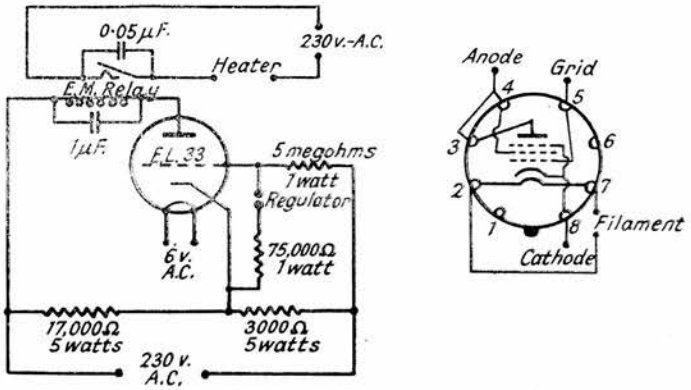
PRINTED IN GREAT BRITAIN AT THE UNIVERSITY PRESS, ABERDEEN

Preprinted from the Journal of the Chemical Society, January 1951, (50), pages 232—233.

50. *An Inexpensive Thermostat Relay.*

By Duncan Taylor.

It has become popular in recent years to employ some type of thyratron relay t
accurate thermostatic control and to reduce the current at the mercury contac
mercury–toluene regulator to not more than a few microamps. The regulator, t
provided that clean mercury is used for the initial filling, has a practically indefinite
not by any means can this be claimed for the thyratron valve. During recent studie
Department on heterogeneous equilibria, accurate, continuous, and reliable ther
control was necessary for six months, and it was found that a thyratron relay coul
relied on to give more than, at most, three months' continuous service. To overcome thi
an inexpensive relay (see figure) was developed, and experience has shown that it
all the desirable features of the thyratron type of relay with a useful life of six mon
tinuous running. Another good feature is that the thermostat heaters are cut off or swi
at the same instant as the regulator contacts close or open, respectively. The general
involved in this relay is well established (cf. Cooke and Swallow, *J. Sci. Instr.*, 1929, **6**,
the circuit illustrated has the advantage of operating from A.C. mains, uses inexpensiv



components and requires no rectifier. The principle is simply that of an electromagn
of the Post Office type in the anode circuit of a valve, the grid potential of which is vari
opening and closing of the regulator contacts.

The electromagnetic relay should have a coil resistance of 1000 Ω and be fitted with he
normally-closed contacts (supplied for example by Londex Ltd., London, S.E.20). The
function satisfactorily in this circuit if the contacts open smartly on the application of 10 v. D
coil. A 1-μF. condenser (750 v. D.C. test) must be connected across the relay coil to prevent c
chatter, and a 0·05-μF. condenser (500 v. D.C. test) connected across the contacts is desirable t
essential as a spark suppressor when the contacts are interrupting a current of about 1 amp.,
using 250-w. heaters. There are no doubt several types of valve which could be used in this ci
the one preferred is a Mullard EL33, an ordinary radio output valve; this is rated to give a
anode current of about 33 ma., and in the circuit above the valve delivers only 13 ma. to the
when the regulator closes. Under-running the valve in this way contributes to its long life on c
usage. The connections to the valve are indicated in the figure. There is no difficulty in obt
necessary resistors, but it was convenient and less expensive to wind the 5-w. resistors from
enamelled resistance wire. The 230 v. A.C. to the network and the 6 v. A.C. to the valve c
supplied from a small mains transformer.

When this circuit was being developed, it seemed at first sight preferable that the relay sh
in the opposite way from that given in the figure, namely, that the relay coil should carry norm
contacts which would close on energising of the coil by opening the regulator contacts. The c
in fact be arranged to operate in this manner, but then some instability is introduced, such t
current is flowing in the relay coil merely touching the regulator contacts with the fingers caus
drop in current which may be sufficient to de-energise the coil. No such unpleasant features
encountered in the circuit as given above.

Acknowledgments are due to Dr. R. Scott for some helpful discussions.

University of Edinburgh. [*Received, September 11th*

Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk.